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CORE IONIZATION OF NITROSOBENZENE-DIMER COMPOUNDS: PHENAZON-DI-N-OXIDE

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The C 1s, N 1s and O 1s XPS spectra of solid phenazon-di-N-oxide (PADNO) are presented in order to further elucidate the effects of intermolecular interactions in molecular solids on the dynamics of the core-ionization process. PADNO can be considered a model compound for an intramolecular cis nitrosobenzene dimer. The observed strong N 1s and O 1s shake-up intensity attenuations in going from the nitrosobenzene monomer to PADNO are discussed in detail based on the results of CNDO/S CI equivalent core calculations. The theoretical core-hole spectral functions are in excellent agreement with experiment. It is shown that the calculated shake-up intensities are strongly dependent on electron correlation.

1. Introduction

Comparisons of the shake-up structure in vapour and solid phase XPS spectra of substituted polar organic molecules have recently demonstrated that the dynamics of the core ionization process depend on the specific substituent interactions of neighboring molecules in the condensed molecular solid (for a review, see, eg., ref. [1]). By modelling specific intermolecular interactions via SCF calculations on molecular clusters, i.e. two interacting molecules, [1–3], it was possible to explain the experimental observations for a variety of systems, i.e. donor–acceptor-substituted [2] and nitroso-substituted [3] aromatic molecules. The latter group of compounds appeared to be particularly interesting because nitroso compounds have been known for a long time to form intermolecular dimers upon condensation into a molecular solid [4–6]. In the case of nitroso compounds the intermolecular interaction is well defined but still sufficiently weak. The nitrosobenzene monomer–dimer system has been used as a model compound to study the influence of solid state interactions on core ionizations in these systems [3]. It was shown [3] that the apparent similarities of the shake-up structure in the vapour and solid phases were caused by quite different interactions, i.e. the observed parallels were accidental. The ON–NO moiety formed via dimerization of nitrosobenzene [3] has been found to be the key moiety in understanding the observed shake-up structures.

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Lüttke showed in 1957 [5] that there exists a cis–trans isomerism for dimerized nitroso compounds (see fig. 1a where R stands for the aromatic ring). The nitrosobenzene dimer, which is formed in the condensed, colourless molecular solid exhibits the characteristics of a cis dimer. It was suggested [4] that the absence of the trans configuration is due to its hypothetical planarity. Such trans planarity would lead to a situation where there is conjugation between the phenyl ring and the NO moiety, thereby weakening the N–N interaction to the point where no N–N bond can be formed. In the cis form, due to steric hindrance, however, the phenyl rings are forced to twist almost perpendicular to the ON–NO plane (see fig. 1b, the ON–NO moiety is still planar within a few degrees), thus effectively eliminating conjugation and allowing dimer formation. Therefore, monomer nitrosobenzene, where the aromatic ring and the NO substituent are in plane, locally, undergoes a structural change upon dimerization. The consequence of this structural change on the substituent core ionization processes in these molecules is a different hole screening mechanism in the dimer (solid) as compared to the monomer (gas) [3]. While the N 1s and O 1s screening π charge is drawn from the benzene ring in the monomer due to the planarity of the system, the ON–NO system provides the screening charge in the dimer. It has been demonstrated [3] that the details of the ON–NO coupling determine the shape of the core hole spectral function. In particular, the relative intensities of the shake-up excitations depend on the strength of the ON–NO interaction in such a fasion, that a weaker coupling induces a higher satellite intensity.

Considering the above discussion, it is interesting to ask what happens to the satellite intensities if the N_2O_2 system is integrated into a more extended π system, where the π coupling between the NO group and the phenyl ring system is not avoided as in the nitrosobenzene dimer. Phenazon-di-N-oxide (PADNO) (see fig. 1c for the structure of the compound) is a candidate that fulfills these requirements. Batich and Donald [7] reported the first XPS study of this molecule without, however, considering shake-up satellites. In the present study we report the experimental core-ionization spectra of PADNO together with a complete theoretical analysis on the basis of MNDO and CNDO/S CI calculations on the neutral ground state and on the manifold of core-ionized states of the system. We show by comparison with the results for the nitrobenzene dimer (fig. 1b) that the observed pronounced attenuation in the shake-up structure on going from the nitrosobenzene dimer to PADNO can be understood by considering the ON–NO interaction in PADNO and electron correlation effects within the N_2O_2 moiety. Our computational results indicate, as suggested earlier, a strong influence of electron correlation on the correct description of the core ionization process.

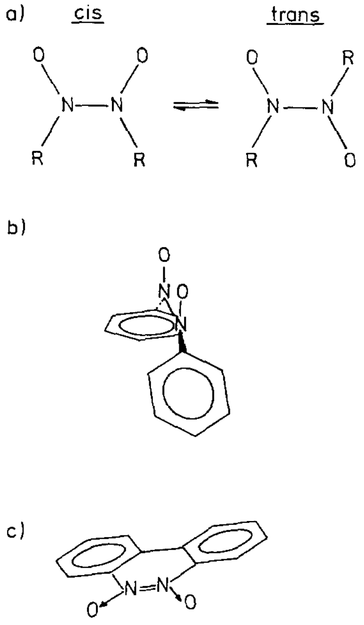


Fig. 1. (a) Cis–trans isomerism for nitroso compound dimers, (b) schematic structure of the nitrosobenzene dimer, (c) schematic structure of phenazon-di-N-oxide.

2. Computational details and results

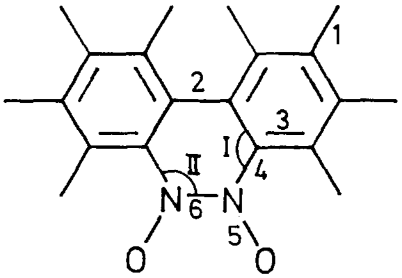
Quantum–chemical calculations were performed within the semi-empirical all-valence-electron closed-shell formalisms of the MNDO [8] and CNDO/S [9] schemes.

The MNDO algorithm was used to carry out potential energy calculations on nitroso biphenyl compounds having different torsion angles around the carbon–carbon bond connecting the two six-membered rings, and also to optimize bond lengths in planar PADNO. MNDO is currently recognized as one of the most reliable tools available in predicting molecular geometries. It normally yields bond lengths and bond angles in excellent agreement with experiment. Torsion angles are somewhat less reliable. As pointed out by Dewar and Thiel [8], molecules containing N–O interactions were not considered in parameterizing MNDO. Thus, NO bonds might not be reproduced with high accuracy.

Based on the geometries optimized using the MNDO scheme, CNDO/S CI [10] calculations using the Pariser–Parr approximation [11] to the two-center repulsion integrals have been carried out to serve two purposes: Firstly, since the CI expansion contained doubly excited configurations the results allowed us to estimate the stability of the SCF calculation against inclusion of electron correlation effects. Secondly, the CI calculations furnish the energies of the electronic excited states. In order to calculate excitation energies in the presence of a core-hole we use the equivalent core approximation [12,13]. In this approximation the atom to be ionized (atomic number Z) is replaced by the next-highest atom in the periodic table ($Z'' = Z + 1$). Excited state calculations were then performed on the "equivalent-core" closed-shell species assuming only singlet coupling between all valence electrons. The 300 lowest energy excitations were selected from 5000 created configurations of proper symmetry [14]. Relative intensities were obtained within the sudden approximation by projection of the correlated ion-state wavefunctions onto that of the "frozen" ion state given in terms of the one-electron orbitals of the neutral system. Projections of the relaxed ion-state wavefunctions onto the correlated and uncorrelated initial state wavefunctions were performed to examine the importance of correlation contributions [15]. Bond orders were calculated according to the Cohen scheme [16,17].

Table 1 summarizes the MNDO bond lengths and bond angles obtained for planar PADNO – this is taken as the reference configuration at $\theta = 0°$ in fig. 2. If the system is then rotated around the torsion angle θ (defined as the angle between the planes of the two six-membered rings), it is found that within the MNDO scheme the system is stabilized at $\theta = 90°$. As is well known for biphenyl compounds the energy of the configuration with $\theta = 180°$ is unfavourable because of H–NO repulsion. In other words, breaking of the N–N bond to yield a dinitroso-substituted biphenyl compound ($\theta = 90°$) is the overall most stable conformation of the system according to MNDO. Note that some points close to the 20° torsion angle have not been explicitly calculated

Table 1
Bond lengths (Å) and bond angles (degree) optimized by MNDO for planar PADNO



No.	Bond/angle	MNDO (PADNO)	Experiment [a] (4,5-dichloro-PADNO)
1	C–H	1.09	–
2	C–C	1.47	≈ 1.47
3	C═C	1.41	≈ 1.38
4	C–N	1.46	1.42
5	N–O	1.22	1.26
6	N–N	1.36	1.33
I	C–C–N	118.42	119.4
II	C–N–N	118.92	120.0

[a] See refs. [18,19].

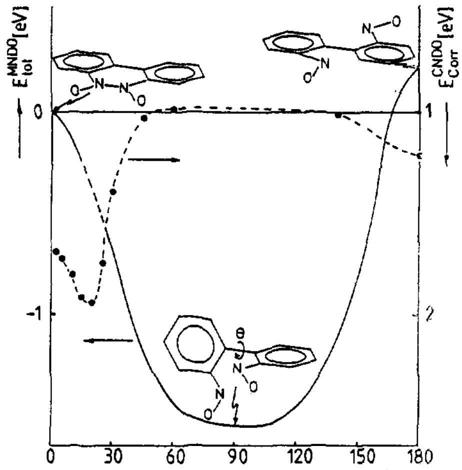


Fig. 2. Potential energy diagram for torsion (*θ*) of the substituted phenyl rings around the connecting C–C bond (energy scale on the left-hand side) as determined by MNDO. The change in electron correlation energy as a function of *θ* is given as the dotted line and refers to the energy scale on the right-hand side.

The results of the present geometry optimization are in contrast to the general assumption that PADNO is a planar molecule [7,18,19]. The calculated structure changes quite dramatically, however, if electron correlation is taken into account. We have tried to simulate this by using the MNDO geometries along the potential energy diagram as input for CNDO/S CI calculations on the neutral molecule. CNDO/S total energy considerations yield energy minima similar to MNDO. Out of this computation we get an estimate of the change in correlation energy along the calculated potential energy curve. The relative correlation energy contribution is shown in fig. 2 by the dotted line. This indicates a much larger error in the calculated relative energy around $\theta = 0°$ than close to $\theta = 90°$ or $\theta = 180°$. We shall discuss the reason for this behaviour and its consequences for the calculated equilibrium geometries in section 4 of the paper.

Fig. 3 and fig. 4 show the calculated spectral functions for the substituent N 1s and O 1s ionization at three different geometries ($\theta = 0°$, $\theta = 15°$, and $\theta = 90°$). Tables 2–5 contain the relevant information on excitation energies and projection amplitudes used to assign and discuss the calculational results.

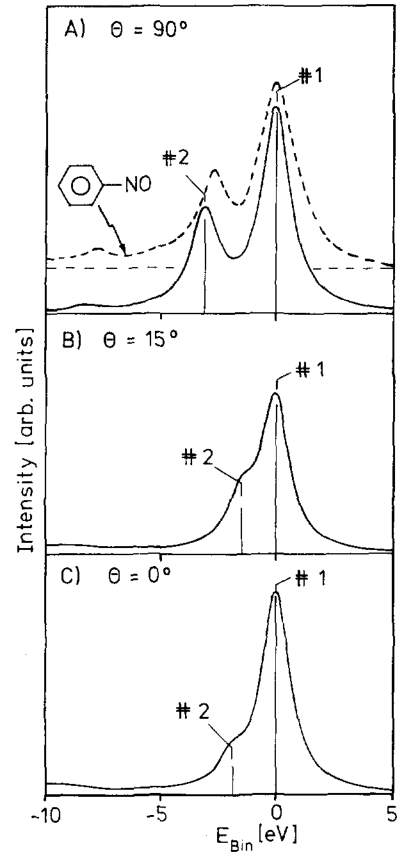


Fig. 3. Calculated spectral functions of N 1s ionizations were each calculated line has been convoluted with a Lorentzian of half-width 1.1 eV for three typical torsion angles *θ*.

3. Experimental details and results

The experimental spectra were taken in a photoelectron spectrometer located at Linköping university. The base pressure of the instrument is less than 1×10^{-10} Torr. The PADNO was kindly provided by Professor W. Lüttke. Samples were prepared in situ by evaporation from a borosilicate tube contained within a simple Knudsen cell, onto a gold substrate held typically at $-80°C$. Evaporation took about 1.5 min at a background

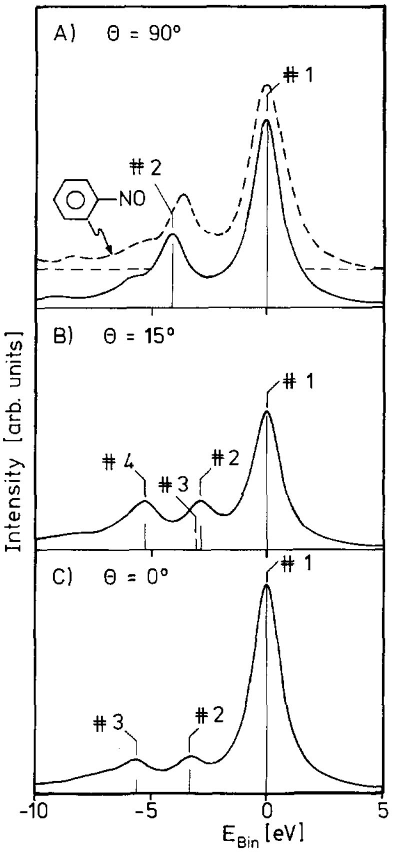


Fig. 4. Calculated spectral functions of O 1s ionizations where each calculated line has been convoluted with a Lorentzian of half-width 1.1 eV for three typical torsion angles θ.

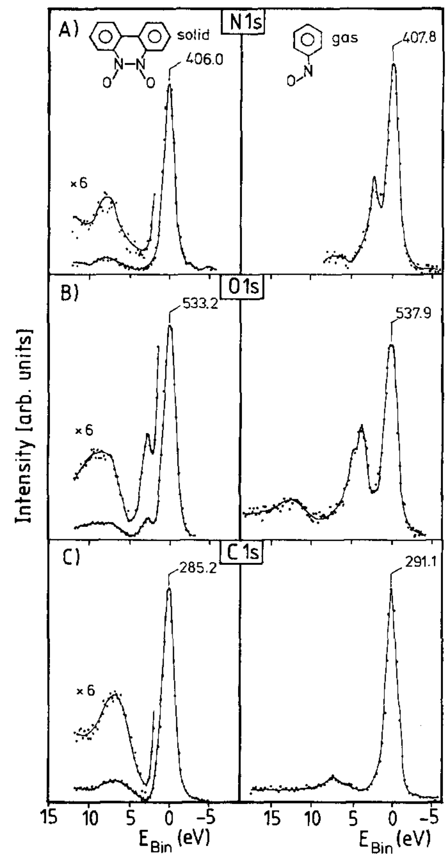


Fig. 5. Core ionization spectra of PADNO (left panels) as compared with corresponding spectra of nitrosobenzene as reported by Slaughter et al. [20] (right panels). The binding energies of the main lines are given in eV.

Table 2

Energies and wavefunctions of the N 1s ion states of PADNO rotamer at $\theta = 90°$, $15°$ and $0°$ as labelled in figs. 3a, 3b and 3c respectively [a)]

θ (deg)	State No.	Energy (eV)	Wavefunction
90	1	−0.648	$0.929\langle 0,0 \Vert 0,0\rangle - 0.248\langle 35,35 \Vert 40,40\rangle + \dots$
	2	2.426	$0.705\langle 0,35 \Vert 40,0\rangle + 0.343\langle 35,35 \Vert 40,40\rangle + 296\langle 0,0 \Vert 0,0\rangle + \dots$
15	1	−0.35	$0.964\langle 0,0 \Vert 0,0\rangle - 0.101\langle 0,38 \Vert 40,0\rangle + \dots$
	2	1.13	$0.705\langle 0,38 \Vert 40,0\rangle - 0.475\langle 0,37 \Vert 40,0\rangle - 0.271\langle 0,35 \Vert 40,0\rangle + \dots$
0	1	−0.53	$0.961\langle 0,0 \Vert 0,0\rangle + \dots$
	2	1.368	$0.680\langle 0,38 \Vert 40,0\rangle + 0.506\langle 0,37 \Vert 40,0\rangle + 0.271\langle 0,36 \Vert 40,0\rangle + \dots$

[a)] The energies are given relative to the uncorrelated core-ionized ground (SCF) state. The wavefunctions are characterized by their CI coefficient and the corresponding determinants are given as a set of four numbers in brackets representing orbitals of the equivalent core ground state. Occupied and unoccupied orbitals are separated by a double bar.

Table 3
Overlap integrals between the ionic and neutral molecule SCF determinants for N 1s ionization

Ion configurations	Overlap with neutral ground state	Overlap with doubly excited configurations as specified	
$\langle 0, 0 \Vert 0, 0\rangle$	0.75681		
$\langle 0, 35 \Vert 40, 0\rangle$	0.20515		
$\langle 35, 35 \Vert 40, 40\rangle$	0.05561		
		$\langle 39, 39 \Vert 40, 40\rangle$	$\langle 39, 39 \Vert 40, 43\rangle$
$\langle 0, 0 \Vert 0, 0\rangle$	0.65717	0.15439	−0.06747
$\langle 0, 38 \Vert 40, 0\rangle$	−0.23639	0.24057	−0.10512
$\langle 0, 37 \Vert 40, 0\rangle$	0.20255	−0.13340	0.05829
$\langle 0, 35 \Vert 40, 0\rangle$	0.03200	−0.03216	0.01405
		$\langle 39, 39 \Vert 40, 40\rangle$	$\langle 39, 39 \Vert 40, 43\rangle$
$\langle 0, 0 \Vert 0, 0\rangle$	0.70294	0.10001	−0.04968
$\langle 0, 38 \Vert 40, 0\rangle$	−0.22077	0.19551	−0.09712
$\langle 0, 37 \Vert 40, 0\rangle$	0.16619	−0.08439	0.04192
$\langle 0, 36 \Vert 40, 0\rangle$	0.07977	−0.09223	0.04581

pressure of 2×10^{-8} Torr in the prepration chamber. Base pressure in the preparation chamber, due to the presence of the highly volatile sample in the Knudsen cell was 2×10^{-9} Torr. In the analysis chamber, however, the vacuum was better than 1×10^{-10} Torr. The spectra were excited by unmonochromatized MgKα radiation. From the relative intensity ratio of substrate and sample signals, and the assumption of an escape depth of 23 Å, as taken from tabulated values for hydrocarbons [20], the thicknesses of the evaporated films were estimated to be in the range of 120 to 140 Å.

Fig. 5 shows the measured C 1s, N 1s and O 1s core-ionization spectra.

4. Discussion

It is useful first to discuss the dinitroso biphenyl compound, i.e. the $\theta = 90°$ rotamer of PADNO. The calculated substituent N 1s and O 1s core-hole spectra of this compound are shown in figs. 3a and 4a. They exhibit the characteristics of the spectra of nitrosobenzene which are given for comparison as dashed curves. In fact, a closer

Table 4
Energies and wavefunctions of the O 1s ion states of PADNO rotamer $\theta = 90°$, $15°$ and $0°$ as labelled in figs. 4a, 4b and 4c, respectively [a]

θ (deg)	State No.	Energy (eV)	Wavefunction
90	1	−0.471	$0.971\langle 0, 0 \Vert 0, 0\rangle - 0.160\langle 35, 35 \Vert 40, 40\rangle + \ldots$
	2	3.615	$0.827\langle 0, 35 \Vert 40, 0\rangle + 0.332\langle 35, 35 \Vert 40, 40\rangle + 0.095\langle 0, 0 \Vert 0, 0\rangle + \ldots$
15	1	−0.496	$0.972\langle 0, 0 \Vert 0, 0\rangle + \ldots$
	2	2.336	$0.696\langle 0, 38 \Vert 40, 0\rangle - 0.456\langle 0, 30 \Vert 40, 0\rangle + 0.255\langle 0, 29 \Vert 40, 0\rangle + \ldots$
	3	2.549	$0.499\langle 0, 38 \Vert 40, 0\rangle - 0.565\langle 0, 30 \Vert 40, 0\rangle - 0.397\langle 0, 37 \Vert 40, 0\rangle + \ldots$
	4	4.760	$0.553\langle 0, 33 \Vert 40, 0\rangle + 0.448\langle 0, 35 \Vert 40, 0\rangle - 0.322\langle 0, 34 \Vert 40, 0\rangle + \ldots$
0	1	−0.796	$0.965\langle 0, 0 \Vert 0, 0\rangle + \ldots$
	2	2.512	$0.851\langle 0, 38 \Vert 40, 0\rangle + 0.222\langle 0, 37 \Vert 40, 0\rangle$
	3	5.081	$0.533\langle 0, 39 \Vert 44, 0\rangle + 0.412\langle 0, 33 \Vert 40, 0\rangle - 0.363\langle 0, 38 \Vert 43, 0\rangle + \ldots$

[a] See footnote to table 2.

Table 5
Overlap integrals between the ionic and neutral molecule SCF determinants for O 1s ionization.

Ion configurations	Overlap with neutral ground state	Overlap with doubly excited configurations as specified	
⟨0, 0 ‖ 0, 0⟩	0.67676		
⟨0, 35 ‖ 40, 0⟩	0.30409		
⟨35, 35 ‖ 40, 40⟩	0.13664		
		⟨39, 39 ‖ 40, 40⟩	⟨39, 39 ‖ 40, 43⟩
⟨0, 0 ‖ 0, 0⟩	0.69447	0.18271	−0.07348
⟨0, 38 ‖ 40, 0⟩	0.15281	−0.19034	0.07654
⟨0, 37 ‖ 40, 0⟩	−0.08859	0.01801	−0.00724
⟨0, 33 ‖ 40, 0⟩	0.25430	−0.20743	0.08342
		⟨39, 39 ‖ 40, 40⟩	⟨39, 39 ‖ 40, 43⟩
⟨0, 0 ‖ 0, 0⟩	0.75197	0.11390	−0.05205
⟨0, 38 ‖ 40, 0⟩	0.13918	−0.15665	0.07159
⟨0, 33 ‖ 40, 0⟩	−0.23949	0.17547	−0.08019
⟨38, 39 ‖ 40, 40⟩	0.00153	0.10035	−0.02736
⟨33, 38 ‖ 40, 40⟩	−0.04433	−0.24134	0.06296

inspection of tables 2–5, and a comparison with the published information on nitrosobenzene [3], shows that there is little difference between the two systems. A detailed analysis reveals that the screening mechanism active in nitrosobenzene is also active in the nitroso-substituted biphenyl: the π charge of the benzene rings, assumed to be coplanar with one nitroso group each, provides the screening charge for the core hole on the substituent. The intense shake-up structure observed upon N 1s and O 1s ionization can be assigned in analogy to nitrosobenzene (see fig. 2 in ref. [3]) to mainly single electron excitations between two orbitals that exhibit relatively large coefficients on the NO moieties. It is well known that the C 1s (ring system) ionizations are not as strongly affected in substituted organics as the substituent ionizations [1]. This result is not too surprising if the relatively small changes in orbital localization on the ring upon formation of the biphenyl system are considered. It was shown previously that the calculated spectral function of nitrosobenzene (figs. 3 and 4) is largely unaffected when electron correlation is included in the calculation. The present computations on the nitroso biphenyl compound reveals the same result. Of course, there is a considerable electron correlation energy contribution to the total energy of the system (see fig. 2), but there is no specific channel that influences the relative correlation energy contributions between the ground and excited states involved in the shake-up and screening processes.

The situation changes when the system assumes a close to planar geometry. The reason for this becomes clear when the bonding in PADNO is considered. The main difference on going from the biphenyl compound to PADNO is the formation of the N–N bond, or a ON–NO interaction. Fig. 6 shows the highest occupied (HOMO) and lowest unoccupied molecular (LUMO) orbitals of the biphenyl compound (with the nitrosobenzene rings artificially turned by 90°) on the left-hand side in comparison with the corresponding orbitals in PADNO on the right-hand side. On going from the dinitroso biphenyl system to PADNO a bonding and an antibonding NO π*–NO π* combination is formed. The N–N bond in PADNO is characterized by occupation of the bonding combination. Obviously, N–N-bond formation does not lead to the creation of a local minimum in the potential energy curve (fig. 2) based on the MNDO calculations. We find this picture to change qualitatively if we consider the effect of electron correlation (fig. 2). The correlation energies were estimated using CNDO/S CI calculations including doubly excited configurations at the MNDO opti-

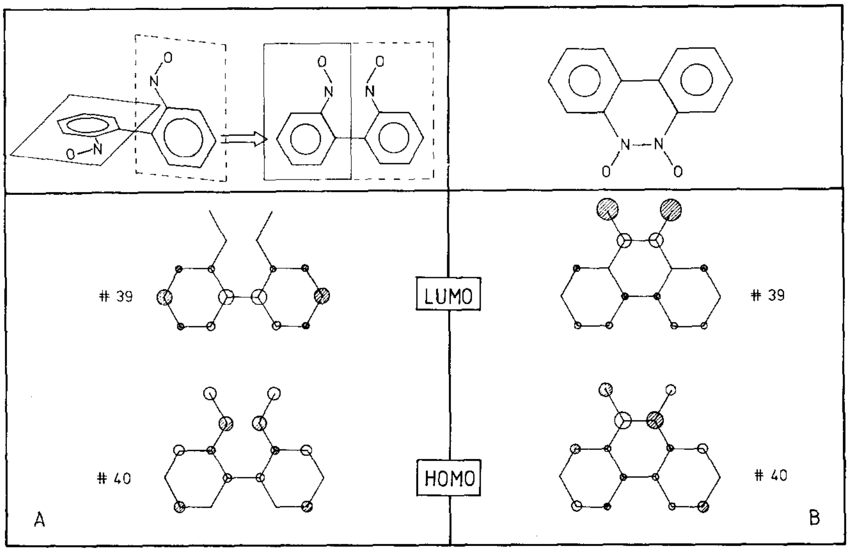


Fig 6. (a) HOMO and LUMO of the bis nitroso biphenyl (left panel) as projected on one common plane, (b) HOMO and LUMO of PADNO.

mized geometries as noted above. Although the correlation energies cannot be used in any quantitative way, they indicate that the correlation energy for the planar geometry is higher, by almost a factor of two than for the biphenyl compounds. Fig. 2 shows a drastic change in the electron energy after rotating the two six-membered rings by more than 20°. This is about the point where the N–N bond can be considered as broken, i.e. both orbital combinations are unoccupied and the system behaves like a biphenyl compound. The reason for the strong influence of electron correlation in the close-to-planar geometry is quite obvious and has been pointed out before in connection with the formation of the nitrosobenzene dimers [3]: the doubly excited configuration involving the HOMO and LUMO levels varies between 4.1 and 5.7 eV above the SCF configuration depending on the torsion angle. Since the doubly excited state leads to a totally symmetric state, i.e. the same symmetry as the ground state, the ground state is stabilized via configuration interaction. The CI stabilization increases if the doubly excited configuration is lowered in energy relative to the SCF state. This will be the case as we elongate the N–N bond by rotating the two benzene rings, i.e. the splitting between bonding and antibonding combination decreases since the NO π^*–NO π^* overlap decreases. Fig. 2 indicates this behaviour. At angles larger than 20°, this correlation contribution disappears, since the NO π^*–NO π^* overlap vanishes and both combinations become unoccupied. With this analysis in mind the MNDO potential energy curve of fig. 2 has to be substantially modified: Even though the absolute correlation contributions along the curve are unknown, we can predict that in addition to the minimum in the MNDO curve at $\theta = 90°$ there will be a second minimum at or close to $\theta = 0°$ due to electron correlation energy contributions. Whether the latter minimum is the global or a local minimum in the curve cannot be determined on the basis of the present results. It is interesting at this point, however, to note that at least within the semi-empirical schemes used here the accepted structure of an organic molecule cannot be reproduced without taking electron correlation effects into account. However, we do not know at present whether the planar structure, determined via X-ray scattering in the solid state (for PADNO derivatives [18,19]) is the minimum-energy structure of the free isolated molecule. Ab initio calculations on this compound could be helpful to further clarify this problem. The existence of a double minimum in this potential energy curve could have some bearing on the chemistry of the compound [21,22].

Fig. 5 shows the core ionization spectra of PADNO in comparison with those of nitrosobenzene [23]. The nitrosobenzene spectra may be taken to represent the spectra of the nitroso biphenyl compound. Firstly, the shifts in binding energies have to be discussed. It has to be recognized that the PADNO spectra are taken on a solid sample, while the nitrosobenzene spectra are gas-phase results. As has been discussed in detail [1] core hole binding energies shift to lower values upon condensing a vapour into a molecular solid due to the extramolecular relaxation contribution [1]. The C 1s spectra which do not show low-energy satellite structure in both cases reflect this shift. The difference in the present case is 5.9 eV in line with these findings. It is known that substituent core ionizations which are not influenced by specific intermolecular interactions, e.g., N 1s (NH_2) in para-nitroaniline (PNA), show a similar behaviour (6.4 eV in the case of N 1s (NH_2) ionization in PNA) [1]. However, the N 1s and O 1s NO ionizations of PADNO experience different shifts, namely 1.8 and 4.7 eV respectively, indicative of the ON–NO bonding interaction. The binding energy difference between N 1s and O 1s ionization ($EB_{O\,1s-N\,1s}$) changes from 130.1 eV in nitrobenzene [25] to 127.2 eV in PADNO. However, this effect cannot be exclusively explained by ON–NO interaction, because the difference in binding energies of the main peaks in gaseous NO and the $(NO)_2$ dimer only changes from 133.0 eV to 133.5 eV [24]. Batich and Donald [7], who actually report a slightly different value for $EB_{O\,1s-N\,1s} = 128$ eV, have argued that the difference in binding energy is due to changes in the polarity of the NO bond introduced by N–N bond formation, e.g., by formation of a $O^{\delta-}$–$N^{\delta+}$–$N^{\delta+}$–$O^{\delta-}$ moiety. Such a polarization shifts the O 1s ionization to lower and the N 1s ionization to higher binding energies. Unfortunately, a detailed comparison of *binding energies* in gaseous and solid nitrosobenzene [25], where the molecule is known to form dimers [26] has yet to be reported.

As done before we shall concentrate here on the main and obvious difference of the nitrosobenzene (gas phase) and PADNO spectra, namely the strong attenuation of shake-up structure in the planar PADNO molecule. The same trend is followed in a comparison of our PADNO and published solid nitrosobenzene spectra [25] (not shown). Again, the latter corresponds to a weakly coupled nitrosobenzene dimer [3]. Comparison of the measured PADNO and nitrosobenzene gas phase spectra with the calculated set in figs. 3 and 4 show surprisingly good agreement. The observed trend in shake-up intensities, as well as the detailed structure of the spectra, is remarkably well reproduced by the calculations. Thus the rest of this section will be devoted to the assignment of the solid PADNO spectra in comparison with the gas phase nitrosobenzene spectra based on the computational results.

As pointed out before, the measured nitrosobenzene gas phase spectra should reflect the spectral functions that we expect for the nitroso biphenyl compound. The assignment of the nitrosobenzene spectrum has already been discussed in some detail [3]. It is sufficient at this point to briefly summarize the results. Upon creation of a core hole on the NO substituent this core hole is screened by valence electrons that originate from the benzene ring and the neighboring N or O atom depending on wether an N 1s electron or an O 1s electron is ejected. We discuss the case of an N 1s hole. The occupied and unoccupied valence orbitals of the core-ionized species are shown in fig. 2 of ref. [3]. Obviously, the occupied orbitals of the core-ionized species contain more NO π^* character than the neutral species. The spectral function calculated by projecting the SCF determinant and mixtures of configurations created from the SCF determinant onto the frozen core hole state created from the neutral ground state determinant is shown in fig. 1 of ref. [3]. This is compared in fig. 3a (dashed curve) with the computations of the present study. They are very similar, as expected. The intense satellite in fig. 3a is predominantly due to a transition between the orbitals with rather large NO π^*-content (orbitals No. 35 and 40 in table 2 correspond to orbitals No. 19 and 21 in nitrosobenzene [3]). Since in the sudden approximation the relative intensities of the ionization peaks are governed by the overlap matrix element it is obvious that both, the ground and this particular excited state exhibit rather large overlap (see table 3). This leads to an intense satellite structure as observed. It should be noted again that the situation in the nitroso biphenyl compound is completely equivalent to nitrosobenzene as far as the calculations are concerned. This is also corroborated by considering the other core ionizations, i.e. O 1s (tables 4, 5 and fig. 4). We feel the comparison between the observed and calculated spectra is convincing, and we do not discuss the result in detail because it would only require repeating the analysis already given for nitrosobenzene [3]. Note that neutral ground state correlation does not significantly contribute to the spectral function.

We are now in a position to address the PADNO core-ionization spectra (fig. 5). Again, the discussion on core ionization of ON–NO dimer compounds [3] can be used to rationalise the experimental observations and the calculational results (figs. 3c and 4c). The wavefunctions of interest for core ionization of the PADNO molecule are given in tables 2–5. The two NO moieties are equivalent in the PADNO neutral ground state. Upon creation of a localized core hole this is no longer the case. We discuss the N 1s core ionization as an example. N 1s ionization leads to a relative localization of the one-electron wavefunctions on specific and different fragments of the molecule (see figs. 7 and 6b). The highest occupied orbital in neutral PADNO is relocalized by N 1s ionization to the NO moiety containing the core hole, i.e. the second HOMO level in the ion state manifold. This implies a charge transfer in the ionized ground state towards the ionized atom. The unoccupied part is localized on the neutral NO moiety. Although the occupied and virtual ion levels are localized on different parts of the N_2O_2 region, their phase relation parallels that of the neutral system orbitals. An excited state of the ion with the LUMO occupied is therefore likely to have a small overlap with the uncorrelated ground state. Also, an electronic excitation which unoccupies the second HOMO, and occupies the LUMO tends to transport the screening charge away from the ionized atom. It is well known that this is unfavourable for intense satellite structure, as has been pointed out by Domcke et al. [27] for the case of *p*-nitroaniline. The correlated ground states, however, contains a determinant where the antibonding N_2O_2 orbital is doubly occupied. The overlap between this component and the excited ion state is therefore expected to increase if we take ground state correlation into account. However, as was already shown in ref. [3], the strength of the ON–NO coupling plays an additional important role in determining the relative satellite intensity. It was pointed out that: (i) if the interaction is weak, the satellite intensity is large, and (ii) if the ON–NO coupling is strong, the satellite intensity is small. Fig. 3b shows the calculated N 1s spectral function for a torsion angle of 15°. Clearly, the shake-up intensity is still moderately high. However, the screening mechanism is modified relative to the nitroso biphenyl compound. Now the screening electrons are also drawn from the non-ionized NO moiety. Inclusion of ground state correlation in the intensity calculation is crucial in this case (see tables 2 and 3). Without ground state correlation the relative satellite intensity for the state around 1.5 eV excitation energy

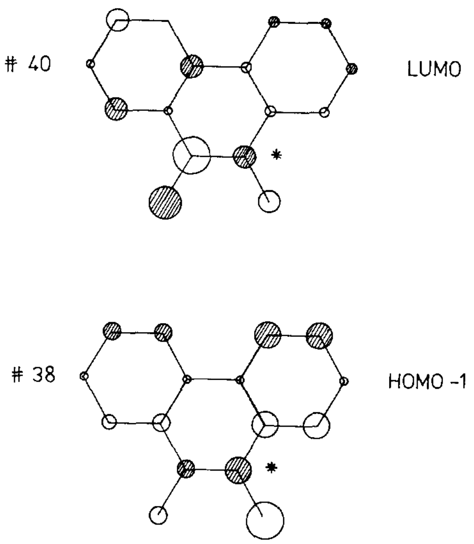


Fig. 7. Highest occupied molecular orbital of N 1s core-ionized PADNO with large NO atomic orbital coefficients, and LUMO of N 1s core-ionized PADNO.

is calculated to be 6.3%. Upon inclusion of ground state correlation, i.e. the abovementioned double excitation, the relative intensity increases to 31.3% (figs. 3b and 4b). This result is qualitatively similar to the result on the nitrosobenzene dimer [3], although the calculated satellite intensity was smaller in the dimer. In the case of the nitrosobenzene dimer discussed in ref. [3], however, the N_2O_2 plane was perpendicular to the benzene ring planes [26]. Under those circumstances the ON–NO coupling was the critical factor determining satellite intensities. In the present case ($\theta = 15°$) the N_2O_2 moiety and the two benzene rings are close to coplanar. This structural difference has to be taken into account. It appears that if we had compared only N–N bond lengths in PADNO (1.33 Å [18,19]) and the nitrosobenzene dimer (1.32 Å [26]) similarities in shake-up intensities according to the rules outlined above would have been expected. Comparison of N–N calculated bond indices for PADNO (1.54) and the nitrosobenzene dimer (1.64), which can be taken as a measure of bond strengths, also suggest this similarity. Figs. 3b and 3c show, however, a pronounced attenuation of the N 1s satellite intensity on going from the nitrosobenzene dimer to PADNO in accord with experiment (fig. 5).

The question now is why does the shake-up intensity drop to 8% in the planar PADNO molecule (see fig. 3c)? This occurs due to changes in the correlation energy contribution. Clearly, for a torsion angle of 15° the HOMO–LUMO splitting on the N_2O_2 moiety leads to a HOMO–LUMO doubly excited configuration 4.1 eV above the ground state. As a consequence the CI ground state contains approximately 20% of that particular configuration (see table 2 for the CI vector). Upon changing the torsion angle to 0° the energy of the corresponding doubly excited configuration increases to 5.8 eV, thereby attenuating the admixture of the doubly excited configuration in the CI neutral ground state from 13% ($\theta = 15°$) to 6% ($\theta = 0°$). This apparently small change has strong consequences for the calculated intensities. The part that is very strongly influenced is the ground state correlation contribution to the intensity. Without ground state correlation in both cases (15° and 0°), the calculated satellite intensity is rather small (6.3% at 15°, and 2.3% at 0°). It increases by inclusion of ground state correlation to 31.3% in the $\theta = 15°$ rotamer, but only to 8.3% for PADNO. The reason for these differences is that the intensity are very sensitive to rather slight changes in the wavefunctions. Thus, by inspection of the magnitude of the CI coefficients and overlap matrix elements given in table 3 it is clear that the changes induced by going from 15° to 0° torsion angle must have a strong effect on the intensities. The excitation energies are much less sensitive to these changes.

Similar results are obtained for the other core ionizations in PADNO. O 1s ionization occurs with a weak satellite, which is in agreement with the calculations. The basic trend towards a weak satellite intensity, however, clearly parallels the situation for N 1s ionization. We note for completeness, without explicitly showing the theoretical results, that the C 1s ionization profiles do not change in any noticeable fashion in line with all observations and calculations reported sofar.

5. Conclusions

We have presented the C 1s, N 1s and O 1s XPS spectra of phenazon-di-N-oxide (PADNO) as a means to model important ON–NO interaction accompanying nitrosobenzene dimerization. In addition, the phenyl rings are coplanar with the N_2O_2 moeity. In contrast, the phenyl ring planes in the nitrosobenzene dimer are perpendicular to the N_2O_2 plane. CNDO/S CI calculations for PADNO core ionizations yield relatively weak satellite peaks in excellent agreement with the experimental spectra. The experimentally observed strong attenuation of satellite (or shake-up) intensity accompanying substituent ionizations in going from nitrosobenzene and the nitrosobenzene dimer to PADNO is reflected by the calculations.

A detailed analysis of the calculations was presented that allowed a determination of the important factors influencing intensity variations. It was shown that the formation of the bonded ON–NO moiety caused changes mainly in the ground state electron correlation contribution to the satellite intensity. The CI calculations indicated that the important correlation contribution comes from a single channel, i.e. a double electron excitation between the occupied bonding and the unoccupied antibonding molecular orbital formed from the NO π^* orbitals on the nitroso substituents upon N–N bond formation in PADNO. It was found that this correlation contribution vanishes on going to the twisted isoelectronic dinitroso biphenyl compound. Breaking of the N–N bond in PADNO to yield the biphenyl compound was shown to generate intense N 1s and O 1s satellite structure characteristic of free nitrosobenzene and the condensed phase cis nitrosobenzene dimer.

It was suggested that neglect of electron correlation contributions in the MNDO geometry optimizations was the reason why the twisted biphenyl structure was calculated to be the most stable configuration, rather than the planar PADNO system.

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