drous sodium methoxide under reflux (oil bath 180°) for 16 h. After cooling, 400 ml water was added and the product was extracted with ether. The extracts were washed six times with aqueous sodium chloride, dried and evaporated to give an oily residue which was purified by prep. TLC. (silica gel, ether/hexane 1:1) and distillation to give 0.12 g (47%) of 1,7a-diaza-7a*H*-indene (**10**) as a colourless oil, bp. 95–98°/22 Torr. – IR. (Film): 1648 s; 1520 s; 1462 m; 1438 s; 1375 s; 1340 s; 1255 s; 1228 s; 1180 m; 1145 m; 1010 m; 920 m; 890 m; 765 s; 740 m. – MS. (70 ev): 118 (100, M^+), 91 (27), 78 (16), 65 (5), 64 (21), 63 (13), 51 (5), 39 (6). – UV. (C_6H_{12}): Max. 338 (510); 310 (1800); 288 (3390); 223 (8340); 221 (8280). Infl. 322 (1380); 300 (1820); 280 (3020). – ^{1}H-NMR. (100 MHz, $CDCl_3$): δ = 8.48/*d*×*d* with fine splitting (J = 1 & 7), 1 pr (H—C(7)); 7.96/*d* with fine splitting (J = 2), 1 pr (H—C(2)); 7.52/*d*×*d* with fine splitting (J = 1 & 9), 1 pr (H—C(4)); 7.06/*d*×*d*×*d* with fine splitting (J = 1 & 7 & 9), 1 pr (H—C(5)); 6.72/*t*×*d* (J = 1.5 & 7), 1 pr (H—C(6)); 6.51/*d*×*d* (J = 1 & 2), 1 pr (H—C(3)). The blue-violet fluorescence in UV. light, the UV.- and the NMR.-spectra of this sample were in complete agreement with those already reported [9].

We thank the MS.-laboratory (direction Prof. *M. Hesse*) for the mass-spectra, the micro-laboratory (direction *H. Frohofer*) for the elemental analyses and the IR.-spectra, and the NMR.-laboratory (direction Prof. *W. v. Philipsborn*) for the NMR.-spectra.

REFERENCES

[1] *J. Heller, A. Yogev & A. S. Dreiding*, Helv. *55*, 1003 (1972).
[2] *G. L. Buchanan, R. A. Raphael, R. Taylor, B. R. O'Connor, H. E. Simmons, J. Heller & A. S. Dreiding*, Helv. *56*, 272 (1973).
[3] *C. B. Chapleo & A. S. Dreiding*, Helv. *57*, 873 (1974).
[4] *L. J. Bellamy*, 'Advances in Infrared Group Frequencies', p. 160, Methuen & Co., 1968; *R. H. Thomson* 'Naturally Occurring Quinones', p. 64, Academic Press, London 1971.
[5] *D. H. R. Barton, P. De Mayo & J. C. Orr*, J. chem. Soc. *1958*, 2239.
[6] *D. H. R. Barton & W. Doering*, 'International Series of Monographs on Organic Chemistry', Vol. 7, p. 61, Pergamon Press, Oxford 1964; *D. H. R. Barton & A. S. Lindsey*, J. chem. Soc. *1951*, 2988.
[7] *W. C. Howell, M. Ktenas & J. M. Macdonald*, Tetrahedron Letters *1964*, 1719.
[8] *M. Gordon, W. C. Howell, C. H. Jackson & J. B. Stothers*, Canad. J. Chemistry *49*, 143 (1971).
[9] *J. D. Bower & G. R. Ramage*, J. chem. Soc. *1957*, 4506; *J. D. Bower*, J. chem. Soc. *1957*, 4510; *P. J. Black, M. L. Hefferman, L. M. Jackman, Q. N. Porter & G. R. Underwood*, Australian J. Chemistry *1964*, 1128; *W. W. Paudler & D. E. Dunham*, J. heterocycl. Chemistry *2*, 410 (1965).

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142. Electronic States of 1,5-Cyclooctadiyne Radical Cation and of Related Systems: The Electronic Structure of *cis*-bent Carbon-Carbon Triple Bonds

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Dedicated to Professor Pl. A. Plattner on his 70th birthday

(10. V. 74)

Summary. The photoelectron spectra of 1,5-cyclooctadiyne (**2**) and of 1,6-dithiacyclodeca-3,8-diyne (**3**) have been recorded. The first four (**2**) or six (**3**) PE. bands have been assigned as follows; in increasing order of ionization potentials:

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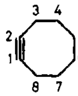
2: $2b_{2g}(\pi)$, $6b_{1u}(\pi)$, $7a_g(\pi)$, $2b_{3u}(\pi)$
3: $14a_g(n)$, $9a_u(\pi)$, $13b_u(n)$, $12b_u(\pi)$, $8b_g(\pi)$, $13a_g(\pi)$

The relative sequence and the positions of the PE. bands are explained in terms of through-bond and through-space interactions between the basis π-orbitals and σ-orbitals of appropriate symmetry behaviour.

An analysis of the PE. spectroscopic data for cyclooctyne (**1**) and for (**2**) indicates that a *cis*-bend of the acetylene moiety by $\theta < 20°$ leads to a split in energy of the in-plane and out-of-plane basis π-orbitals which is smaller than ~ 0.2 eV. This is in agreement with the predictions derived from semiempirical models (MINDO/2, SPINDO) and qualitative orbital arguments. However, it is shown by using orbital localization procedures, that the rationales underlying the two semiempirical models differ significantly.

Some time ago [1] we drew attention to the fact that photoelectron (PE.) spectroscopy is a surprisingly poor tool for gathering information about deformed π-bonds. In particular it was shown that the strong *cis*-bend of the CH_2CCCH_2 moiety in cyclooctyne (**1**) does not lead to a recognizable split between the two PE.-bands corresponding to the ejection of an electron from one or the other of the π-orbitals $16a(\pi)$ and $14b(\pi)$, which, for symmetry reasons, are no longer degenerate. In the present communication we report and analyze in more detail the PE.-data for **1**, for 1,5-cyclooctadiyne (**2**), a rather remarkable molecule recently prepared in our laboratories [2], and for 1,6-dithiacyclodeca-3,8-diyne (**3**) [3]. For comparison we shall refer to the PE. spectroscopic results concerning 3,3,7,7-tetramethylcycloheptyne (**5**) obtained recently by *Schmidt, Schweig & Krebs* [4][2]).



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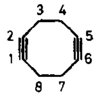

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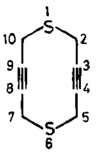

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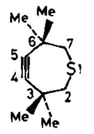

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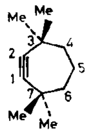

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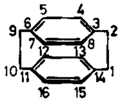
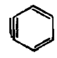


6

$Me(CH_2)_n{-}C{\equiv}C{-}(CH_2)_nMe$
n=1 **7**
n=3 **8**



9

Experimental Results

Molecular Structures. – *Haase & Krebs* have shown by electron diffraction [5] that **1** assumes a twist conformation of C_2 symmetry in which the centres C(8)C(1)C(2)C(3) lie in a plane. The angle C(1)C(2)C(3) is 158.5° ± 0.9°, so that the bond C(2)C(3) deviates by 21.5° from the axis of the triple bond C(1)C(2), the length of which is 1.232 ± 0.006 Å.

The X-ray analysis of the monoclinic crystals of **2** (space group $P2_1/c$; 2 molecules in the unit cell) by *Römming* [6] shows that the molecule belongs at least to C_i. However, the maximum deviations from coplanarity of all carbon centres is only

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[2]) We thank Dr. *A. Krebs* for kindly having made these data available, prior to their publication.

0.023 Å so that for all practical purposes we may classify the molecule as belonging to D_{2h}. The angle C(1)C(2)C(3) is within the limits of error the same as in **1**, *i.e.* 159.1° ± 0.3° (deviation of bond C(2)C(3) from triple bond C(1)C(2) axis 20.9°) and the C(2)C(3)C(4) angle is 110.8° ± 0.3°. The triple bond length is shorter than in **1**, namely 1.185 ± 0.005 Å, and the distance between the two triple bonds (*i.e.* C(1)....C(6)) is only 2.569 Å, *i.e.* less than the distance of 2.78 Å between the pairs of apical carbon atoms C(3)....C(14) and C(6)....C(11) in [2,2]paracyclophane (**6**) [7]. (Distance C(4)....C(13) etc. = 3.09 Å).

X-ray analysis of the monoclinic crystals of **3** (space group $P2_1/c$; 2 molecules in the unit cell) by *Eglinton, Lardy, Raphael & Sim* [3] indicates that the molecule is centrosymmetric and assumes most probably a chair-like conformation of C_{2h} symmetry. No detailed parameters are given, but the electron density map (projected along the b-axis) shown in [3] suggests that the CH_2CCCH_2 moiety is only slightly bent and twisted, that the distance C(3)....C(9) between the two triple bonds exceeds ~3 Å (*i.e.* of same size as C(4)....C(13) in **6**) and that the bond C(2)C(3) deviates by approximately 5° from the triple bond axis C(3)C(4).

In Fig. 1 are shown diagrams of the structures for **1**, **2** and **3** and the definitions relative to the molecular framework, of the coordinate systems used in this communication.

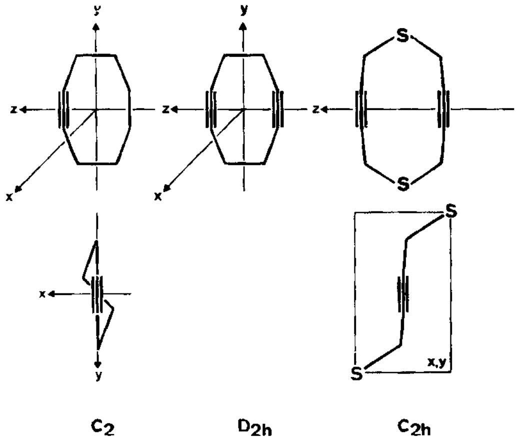

Fig. 1. *Conformations and definition of the axes for* **1**, **2** *and* **3**

Photoelectron-Spectra. – In Figure 2 and 3 are shown the HeI PE. spectra of **1**, **2** and **3**. The vertical ionization potentials I_v given in Table 1, are the positions I_{max} of the maxima of the *Franck-Condon* envelopes of the bands: $I_v = I_{max}$ (mean error approximately ±0.02 eV). The PE. spectra have been recorded on a homebuilt instrument modeled on the specifications given by *Turner* [8]. To discriminate between those PE. bands in the spectrum of **3** which are due either to ejection from the π-orbitals $13a_g(\pi)$, $9a_u(\pi)$, $8b_g(\pi)$, $12b_u(\pi)$ or from the sulfur lone-pair orbitals $14a_g(n)$, $13b_u(n)$, a spectrum using HeII radiation has been recorded (see Figure 3), sacrifying some of the resolution in favour of higher counting rates.

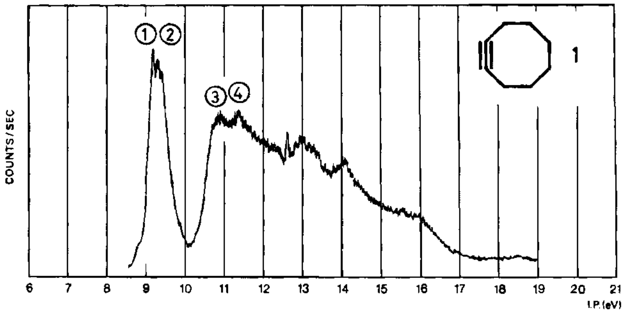

Fig. 2. *HeI PE. spectrum of cyclooctyne* (**1**)

Table 1. *Vertical ionization potentials* (eV) *of cyclooctyne* (**1**), *1,5-cyclooctadiyne* (**2**) *and of 1,6-dithiacyclodeca-3,8-diyne* (**3**)

	1			**2**		**3**	
Band	Orb. (C_2)	Orb. (C_{2v})	I_v	Orb.	I_v	Orb.	I_v
①	14b(π)	$4b_1(\pi)$	9.18^b	$2b_{2g}(\pi)$	9.16^b	$14a_g(n_-)^f$	8.73
②	16a(π)	$13a_1(\pi)$	$(9.30)^c$	$6b_{1u}(\pi)$	9.3_0	$9a_u(\pi_{z,+})$	
③	$15a(\sigma)^a$	$12a_1(\sigma)^a$	10.9	$7a_g(\pi)$	$(9.7_5)^e$	$13b_u(n_+)$	
④	$13b(\sigma)^a$	$10b_2(\sigma)^a$	11.4	$2b_{3u}(\pi)$	10.07	$12b_u(\pi_{xy,+})^f$	9.6_0
⑤				$(\sigma)^d$	13.0	$8b_g(\pi_{xy,-})$	
⑥						$13a_g(\pi_{z,-})$	10.31
⑦						$(\sigma)^g$	11.8
⑧						$(\sigma)^g$	12.2

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[a] Assignment according to the results of MINDO/2 and SPINDO calculations (see Tab. 2).
[b] Adiabatic potential (band onset) at 8.9 eV.
[c] Second prominent feature of the composite band (vibrational v ← 0 component of first and/or 0 ← 0 component of second band ?)
[d] Assignment unknown (see Tab. 2).
[e] Value uncertain because of strong overlap with the first two bands.
[f] Sequence according to EHT calculation.
[g] Assignment unknown.

Orbitals. – In the following we shall use the approximation embodied in *Koopmans'* theorem, *i.e.* discussing electronic states ${}^2\psi_j$ of the radical cations M^+ in terms of the canonical orbitals ψ_i of the parent ground state molecule M. This implies that all orbitals ψ_i including the one (ψ_j) vacated in the process

$$M + h\nu \rightarrow M^+ ({}^2\psi_j) + e^- \qquad (1)$$

are assumed to remain frozen during the ejection process.

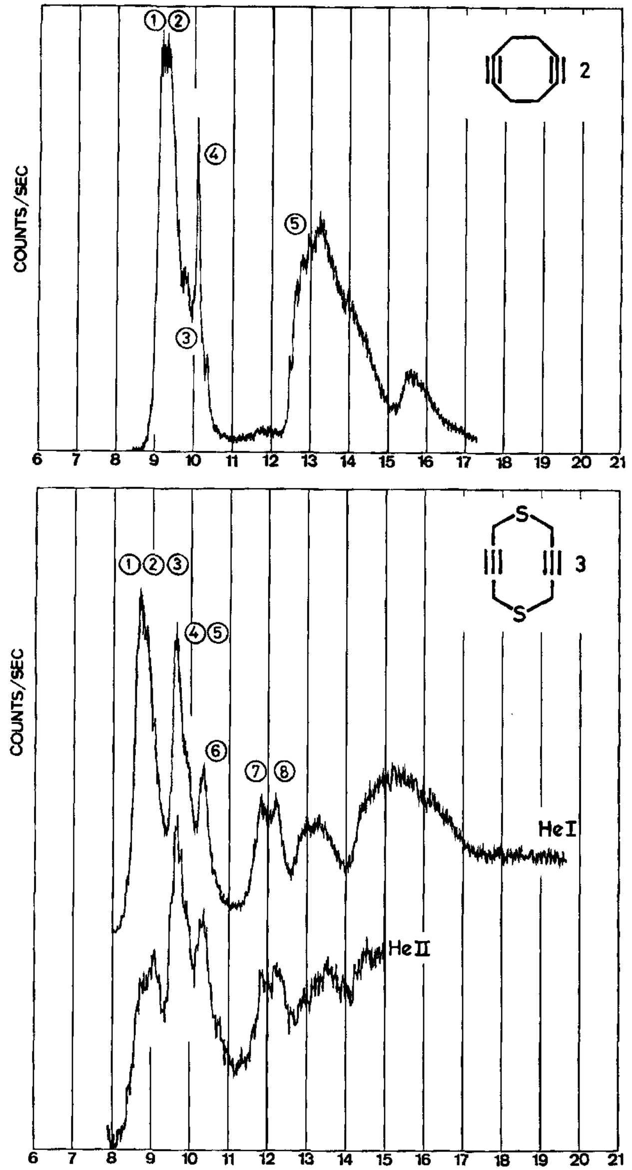


Fig. 3. *HeI PE. spectrum of 1,5-cyclooctadiyne* (**2**) *and HeI/HeII spectra of 1,6-dithiacyclodeca-3,8-diyne* (**3**)

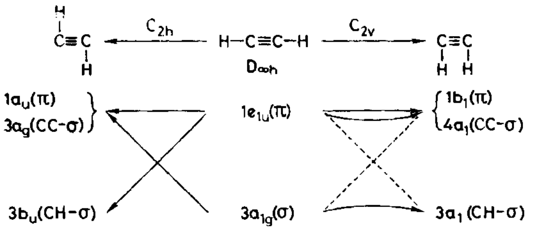
The orbitals ψ_j of **1**, **2** and **3** are labelled according to the symmetry groups C_2, D_{2h} and C_{2h} respectively (*cf.* Figure 1 for the definition of the axes). For **1** the labels relative to a hypothetical C_{2v} structure are included to make easier the correlation with the orbitals of **2**. The sets of doubly occupied orbitals (including all inner shell orbitals) are:

$$\begin{array}{lll} \mathbf{1} & C_2: & \overbrace{13 \times A_1 + 3 \times A_2}^{16 \times A} + \overbrace{4 \times B_1 + 10 \times B_2}^{14 \times B} \\ & C_{2v}: & \\ \mathbf{2} & D_{2h}: & 7 \times A_g + B_{1g} + 2 \times B_{2g} + 4 \times B_{3g} \\ & & + A_u + 6 \times B_{1u} + 5 \times B_{2u} + 2 \times B_{3u} \\ \mathbf{3} & C_{2h}: & 14 \times A_g + 9 \times A_u + 8 \times B_g + 13 \times B_u \end{array} \qquad (2)$$

This list fixes the numbers of the highest occupied orbitals belonging to each of the irreducible representations, in particular of those to which the basis bond orbitals π_x and π_z (or π_{yz}) contribute with greatest weight. In the case of **3** one has to consider in addition to the π-dominated orbitals those molecular orbitals which are mainly centred on the $3p_{xy}$ AOs of the sulfur atoms, *i.e.* the so called lone-pair orbitals, the orbital energies of which fall into the range of the π-orbital energies.

Cyclooctyne (1). – The PE. spectrum of **1** (Fig. 2) exhibits a narrow π-band ①, ② at $I_v(\pi) = 9.2$ eV ($I_a(\pi) \approx 8.9$ eV) with a halfwidth (HW) of only 0.6 eV [1]. This is of the same size as that of the corresponding π-bands in the PE. spectra of diethylacetylene (**7**) ($I_v(\pi) = 9.25$ eV; HW = 0.5 eV) or di-*n*-butylacetylene (**8**) ($I_v(\pi) = 9.06$ eV; HW = 0.5 eV) [9] in which the degeneracy of the π-orbitals is only slightly disturbed by the asymmetry introduced by the terminal alkyl substituents. Therefore the difference $\Delta\varepsilon(\pi) = |\,\varepsilon(16a(\pi)) - \varepsilon(14b(\pi))\,|$ between the orbital energies of the π-orbitals in **1** can not be larger than a vibrational quantum of the ionized triple bond, *i.e.* $\tilde{\nu} \approx 1600\ \mathrm{cm}^{-1}$ or ≈ 0.2 eV [10]. In view of the substantial σ-π-mixing which must necessarily occur as a consequence of the deviation by ~20° of the C(1)C(2) and C(2)C(3) bonds from collinearity, this is a rather surprising result, which merits a few comments.

Model calculations which show the influence of bending on the orbital structure of acetylene HCC-angle = π-θ have been performed by *Hoffmann, Imamura & Hehre* [11] using the Extended *Hückel* Theory [12] and more recently with the MINDO/2 procedure [13] by *Haselbach* [14] in the course of a theoretical investigation of 1,2-benzyne (**9**). Their arguments can be summarized qualitatively as shown in (3):



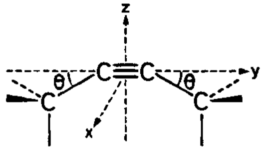
(3)

We are using e_{1u} and a_{1g} instead of π_u and σ_g^+ for the orbitals of acetylene ($D_{\infty h}$) to avoid confusion with the usual chemical σ, π-terminology.

The rationalization suggested is that a *trans*-bend ($D_{\infty h} \rightarrow C_{2h}$) will lead to a lowering of the in-plane component of $1e_u(\pi)$, which for an angle $\theta = 90°$ will end up as the out-of-phase linear combination $3b_u$(CH-σ) of the CH-σ-orbitals, whereas the $3a_g(\sigma)$ orbital of acetylene becomes the $3a_g$(CC-σ) of the bent model system. The two orbitals $3b_u$(CH-σ) and $3a_g$(CC-σ), being respectively u and g relative to inversion, are allowed to cross for an intermediate angle θ as indicated in (3). On the other hand under a *cis*-type deformation ($D_{\infty h} \rightarrow C_{2v}$) the corresponding orbitals $4a_1$(CC-σ) and $3a_1$(CH-σ) emanating from $1e_u(\pi)$ and $3a_g(\sigma)$ respectively, belong to the same irreducible representation A_1 of C_{2v}. Consequently the non-crossing rule applies and the corresponding orbital energies change only little in function of θ, as indicated on the right hand side of (3). In particular for small values of θ the two orbitals dominantly π in character remain close in energy, which suggests that we should expect only a small split between the two PE. bands due to electron-ejection from these two highest occupied orbitals.

An important assumption underlying the above argument is that the orbitals $1a_u(\pi)$, $3a_g$(CC-σ) for the C_{2h} system and $1b_1(\pi)$, $4a_1$(CC-σ) for the C_{2v} system are almost accidentally degenerate for θ = 90°, as suggested by the theoretical results obtained by *Haselbach* [14]. It should be mentioned that the argument embodied in (3) is similar to the one given by *Gimarc* [15] for the dependence on θ of the orbital energies of diimide. It is also in agreement with the *ab initio* calculations carried out by *Millie, Praud & Serre* [16].

To support this argument in the particular case of an alkyl-substituted triple bond (*e.g.* **1**) we have carried out MINDO/2 [13] and SPINDO [17] calculations for a symmetrically bent dimethylacetylene of C_{2v} symmetry within the range of bending angles $0 \leq \theta \leq 30°$. The assumed conformations are shown in (4), *i.e.* starting from D_{3h} for θ = 0°:



(4)

From the data summarized in Table 2 it follows:

Table 2. *Results of* MINDO/2 *and* SPINDO *calculations for a* cis-*bent dimethylacetylene*. Assumed conformation as shown in (4). θ = angle between C(3) C(4) bond and y-axis. All orbital energies in eV

Orb. (D_{3h})	0°	10°	20°	30°	Orb. (C_{2v})
			MINDO/2		
2e'(π)	- 9.66	- 9.60	- 9.45	- 9.24	$7a_1$(π)
		- 9.66	- 9.65	- 9.64	$2b_1$(π)
$5a'_1$(σ)	-11.24	-11.28	-11.37	-11.50	$6a_1$(σ)
1e"(σ)	-13.54	-13.52	-13.45	-13.30	$5b_2$(σ)
		-13.54	-13.55	-13.56	$1a_2$(σ)
			SPINDO		
2e'(π)	-10.07	-10.08	-10.10	-10.15	$2b_1$(π)
		-10.09	-10.17	-10.29	$7a_1$(π)
1e"(σ)	-14.31	-14.30	-14.28	-14.21	$5b_2$(σ)
		-14.31	-14.31	-14.32	$1a_2$(σ)
$5a'_1$(σ)	-14.53	-14.51	-14.46	-14.40	$6a_1$(σ)

a) The orbital energies $\varepsilon(\psi_j)$ of the orbitals $7a_1$ and $2b_1$ ($\theta > 0°$) emanating from $2e'(\pi)$ for $\theta = 0°$ (*i.e.* the orbitals corresponding to $4a_1$(CC-σ) and $1b_1(\pi)$ of a *cis*-bent acetylene given in (3)) are predicted to differ by $\Delta\varepsilon = \varepsilon(7a_1) - \varepsilon(2b_1)$ as shown in (5) in function of θ (values in eV):

	θ:	0°	10°	20°	30°
MINDO/2:	$\Delta\varepsilon$:	0.00	0.06	0.20	0.40
SPINDO:	$\Delta\varepsilon$:	0.00	−0.01	−0.07	−0.14

(5)

As can be seen both methods suggest that for $\theta < 20°$ the split $\Delta\varepsilon$ is less than 0.2 eV. In view of this small split the reversal in ordering ($7a_1$ above $2b_1$ in MINDO/2, $2b_1$ above $7a_1$ in SPINDO) seems at first hardly significant. For larger values of $\theta \approx 30°$ the difference $\Delta\varepsilon$ is predicted to be of the order of 0.40 eV by MINDO/2 and −0.14 eV by SPINDO, *i.e.* of a size leading to a measurable split between the two components of the π-band in the PE. spectrum. This is what has been observed by *Schmidt, Schweig & Krebs* [4], who found $\Delta\varepsilon = 0.31$ eV and 0.32 eV for **4** and **5** respectively. From the correlation diagram shown in (3) one would conclude that the sequence $2b_1$ above $7a_1$ is presumably more reasonable in agreement with the results of the SPINDO calculation. However, this particular sequence should be considered only as a working hypothesis, until additional supporting experimental evidence is available.

b) Although both models seem to agree in as far as the lack of a split in the π-band of the PE. spectrum of **1** is concerned, the underlying 'philosophy' is quite different, as can be shown by subjecting the set of canonical orbitals ψ_j of dimethylacetylene to an *Edmiston-Ruedenberg* localization procedure [18]. It is found that the selfenergies $\alpha(\pi)$ of the localized π-orbitals $\pi_{y,z}$ and π_x belonging to the irreducible representations A_1 and B_1 derived from the MINDO/2 model, are practicalyl equal in the range $0 \leq \theta \leq 30°$, whereas those obtained from the SPINDO procedure yield $\alpha(\pi_{y,z})$ well below $\alpha(\pi_x)$ for larger values of θ (values in eV):

		0°	10°	20°	30°	
MINDO/2:	$\alpha(\pi_x)$	−10.87	−10.87	−10.86	−10.85	(B_1)
	$\alpha(\pi_{y,z})$	−10.87	−10.87	−10.89	−10.91	(A_1)
	$\varkappa$	0.00	0.51	1.02	1.57	
SPINDO:	$\alpha(\pi_x)$	−10.71	−10.73	−10.76	−10.82	(B_1)
	$\alpha(\pi_{y,z})$	−10.71	−10.85	−11.23	−11.80	(A_1)
	$\varkappa$	0.00	1.12	2.14	2.99	

(6)

On the other hand the bond-orbital/bond-orbital interaction term $\varkappa$ between $\pi_{y,z}$ and the central CC-σ-orbital is twice as large for the SPINDO than for the MINDO/2 model. As a result, the close agreement between the two methods as far as the result $\Delta\varepsilon \approx 0$ for $\theta < \sim 20°$ is concerned is the outcome of two different assumptions: Whereas MINDO/2 assumes almost degenerate selfenergies $\alpha(\pi)$ for π_x and $\pi_{y,z}$ with little interaction of the latter with CC-σ, SPINDO postulates a large gap $\alpha(\pi_x) - \alpha(\pi_{y,z})$ which is compensated by the strong interaction of $\pi_{y,z}$ with CC-σ-

Irrespective of this difference in genesis the resulting canonical orbitals $7a_1$ and $2b_1$ of a *cis*-bent dimethylacetylene with $\theta \approx 20°$ – and thus of the π-orbitals in **1** – can be rationalized qualitatively in a manner closely resembling the arguments given by *Radom, Pople & Mock* [19] for twisted double bonds. A plot of the $7a_1$ orbital of dimethylacetylene (similar to those shown in Figure 7 for the canonical π-orbitals of **2**) indicates that for $\theta = 20°$ this is still essentially a π-type orbital, which however bulges away from the bend of the CCCC moiety, *i.e.* in the direction of the z-axis shown in Figure 1. This deformation has two consequences: 1) The interaction between the no longer parallel $2p_{y,z}$-AOs at the centres 2 and 3 decreases, which raises the $7a_1$-orbital relative to the $2b_1$ (π_x) orbital, and 2) the admixture of 2s will lower its energy. Obviously both effects tend to compensate each other, so that $\varepsilon(7a_1)$ is practically equal to $\varepsilon(2b_1)$ as indicated by the PE. spectrum of **1**.

Table 3 contains the results of the MINDO/2 and SPINDO calculations for **1** (C_2 structure according to [5]). In agreement with the model calculations for a *cis*-bent dimethylacetylene, the two highest occupied orbitals of **1** are again of π-type ($16a(\pi)$, $14b(\pi)$) and nearly degenerate. The differences $\varepsilon(16a(\pi)) - \varepsilon(14b(\pi)) = 0.07$ or -0.13 eV, depending on the model, are less than a vibrational quantum of the (C≡C) mode (~0.2 eV). Thus the calculations explain, why no split is observed for the

Table 3. *Valence-shell orbitals and orbital energies* ε (ψ_j) (in eV) *of cyclooctyne* (**1**) *and 1,5-cyclooctadiyne* (**2**) *according to the MINDO/2 and SPINDO models.* Structures: **1** [5]; **2** [6]. Parameters: MINDO/2: [13]; SPINDO: [17]. Only the orbitals with energies above –16 eV are given

	Cyclooctyne (**1**)					1,5-Cyclooctadiyne (**2**)			
	MINDO/2		SPINDO			MINDO/2		SPINDO	
j	$\varepsilon(\psi_j)$	ψ_j	$\varepsilon(\psi_j)$	ψ_j	j	$\varepsilon(\psi_j)$	ψ_j	$\varepsilon(\psi_j)$	ψ_j
22	-9.13	$16a(\pi)$	-9.84	$14b(\pi)$	20	-9.20	$2b_{2g}(\pi)$	-10.04	$2b_{2g}(\pi)$
21	-9.21	$14b(\pi)$	-9.97	$16a(\pi)$	19	-9.33	$6b_{1u}(\pi)$	-10.29	$6b_{1u}(\pi)$
					18	-9.50	$7a_g(\pi)$	-10.32	$7a_g(\pi)$
					17	-10.14	$2b_{3u}(\pi)$	-10.37	$2b_{3u}(\pi)$
20	-9.93	15a	-11.79	15a	16	-10.49	$5b_{1u}$	-13.12	$1a_u$
19	-10.53	13b	-12.19	13b	15	-11.66	$6a_g$	-13.45	$5b_{1u}$
18	-11.12	14a	-12.34	14a	14	-11.72	$1a_u$	-13.71	$1b_{2g}$
17	-11.22	13a	-12.81	12b	13	-12.74	$5b_{2u}$	-13.94	$5b_{2u}$
16	-11.76	12b	-13.31	13a	12	-12.95	$1b_{2g}$	-14.32	$4b_{3g}$
15	-12.26	12a	-13.39	12a	11	-13.18	$4b_{3g}$	-14.71	$6a_g$
14	-12.42	11b	-13.65	11b	10	-15.13	$5a_g$	-15.79	$5a_g$
13	-12.45	11a	-14.45	10b	9	-15.72	$1b_{1g}$	-15.82	$1b_{1g}$
12	-13.27	10b	-14.49	11a					
11	-15.08	9b	-15.40	9b					
10	-15.88	10a	-15.95	10a					

π-band in the PE. spectrum of **1**. At the same time they provide a welcome test for the conclusions drawn in the previous paragraph. Note again the reversal of the two π-orbitals in going from the MINDO/2 (16a(π) above 14b(π)) to the SPINDO (14b(π) above 16a(π)) model.

The π-bands ① and ② are followed by a wide σ-band system, the first two prominent maxima of which are ③ at 10.9 eV and ④ at 11.4 eV. According to the MINDO/2 and SPINDO calculations (see Tab. 3) one would assign them to electron removal from the σ-orbitals 15a(σ) and 13b(σ) respectively. Numerically the MINDO/2 predictions (−9.93 and −10.53 eV) are closer to the observed band positions than those derived from the SPINDO model. However, in view of the known shortcomings of the former procedure, the agreement may well be fortuitous.

1,5-Cyclooctadiyne (2). – This molecule provides an ideal example for the application of the heuristically useful concept of 'through-space' ('th.sp.') and ,through-bond' ('th.b.') coupling between semi-localized orbitals, as introduced by *Hoffmann* [20]. The PE. spectrum of **2**, given in Fig. 3 shows four π-bands, three of which, ①, ② and ③ strongly overlap in the region of 9 to 9.5 eV, and a fourth band ④ near 10 eV. That these bands must necessarily be the π-bands is obvious from a consideration of the shifts towards higher ionization potentials which the onset of the σ-band system suffers along the series cyclooctane ($I_{\sigma,\,Ons.}$ = 10.2 eV), **1** ($I_{\sigma,\,Ons.}$ = 10.8 eV), **2** ($I_{\sigma,\,Ons.}$ = 12.5 eV) as a consequence of increasing unsaturation. This trend is quite general and has been discussed previously, *e.g.* [21].

The results of MINDO/2 and SPINDO calculations for **2**, summarized in Table 3, suggest that the sequence of the molecular orbitals corresponding to ①, ②, ③ and ④ is $2b_{2g}(\pi)$ (= HOMO), $6b_{1u}(\pi)$, $7a_g(\pi)$, $2b_{3u}(\pi)$. According to MINDO/2 the first three orbitals should lie close together, well separated from the fourth, whereas SPINDO predicts that all four of them are closely grouped together with a gap of ∼3 eV separating them from the following σ-orbitals.

In Figure 4 are shown qualitative representations of these four π-orbitals, which are dominated by the following linear combinations of the basis π-orbitals of the triple bonds:

$$\begin{aligned}
\pi_{x,-} &= (\pi_{x,1} - \pi_{x,5})/\sqrt{2} \rightarrow 2b_{2g}(\pi)\\
\pi_{z,+} &= (\pi_{z,1} + \pi_{z,5})/\sqrt{2} \rightarrow 6b_{1u}(\pi)\\
\pi_{z,-} &= (\pi_{z,1} - \pi_{z,5})/\sqrt{2} \rightarrow 7a_g(\pi)\\
\pi_{x,+} &= (\pi_{x,1} + \pi_{x,5})/\sqrt{2} \rightarrow 2b_{3u}(\pi)
\end{aligned} \tag{7}$$

Note that the sign in the linear combinations $\pi_{z,+}$ and $\pi_{z,-}$ corresponds to the definition that $\pi_{z,1}$ and $\pi_{z,5}$ are both oriented identically with respect to the z-axis.

On the basis of the arguments given in the previous section, one expects that the orbital energies $\alpha(\pi)$ of the basis π-orbitals are practically degenerate: $\alpha(\pi_{x,1}) = \alpha(\pi_{x,5}) \approx \alpha(\pi_{z,1}) = \alpha(\pi_{z,5})$. On the other hand the orbital energies of the linear combinations (7) must all be different, because of the differences in overlap, and thus in 'through-space' interaction of the $\pi_{x,\mu}$ and the $\pi_{z,\mu}$ basis orbitals. For a distance R = 2.569 Å the overlaps between carbon 2p AOs in positions 1,6 (*Slater* exponent 1.625) are $S_\pi = \langle 2p\pi|2p\pi\rangle = 0.0249$ and $S_\sigma = \langle 2p\sigma|2p\sigma\rangle = 0.1132$ [22], *i.e.*

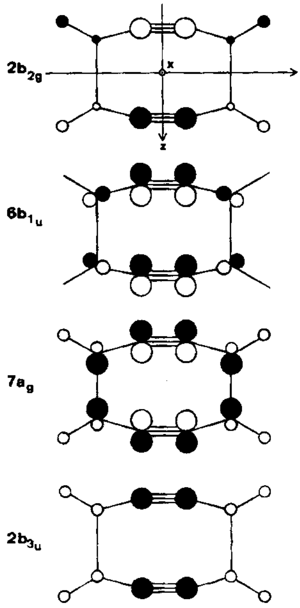


Fig. 4. *Schematic representation of the π-molecular orbitals of 1,5-cyclooctadiyne* (**2**). Note that in $2b_{2g}$ and $2b_{3u}$ the circles on the methylene groups characterize the pseudo-π orbitals, which are antisymmetric with respect to the y, z plane, whereas in $6b_{1u}$ and $7a_g$ the 1s-linear combinations of these groups are symmetrical

$S_\sigma/S_\pi = 4.61$. Consequently the absolute value of the split between the linear combinations $\pi_{z,-}$ and $\pi_{z,+}$ must be much larger than between $\pi_{x,-}$ and $\pi_{x,+}$ (ratio $\sim$4.6 according to the naive overlap criterion), leading to the ordering shown qualitatively in Figure 5 (level after 'th. sp.').

In principle each of the linear combinations (7) can interact with lower lying σ-orbitals of the same symmetry species. However, qualitative arguments suggest that only $\pi_{z,-}$ (irreducible representation A_g) and $\pi_{x,-}$ (irreducible representation B_{2g}) will find energetically close lying σ-orbitals of the same symmetry. These are the orbitals centred mainly on the CC-σ-bond orbitals of the 3,4 and 7,8 CC-bonds (A_g) and on the pseudo-π combination of the CH_2 orbitals (B_{2g}) respectively. The $\pi_{x,+}$ linear combination interacts to a smaller degree with the linear combination of the pseudo-π CH_2 orbitals of B_{3u} symmetry, which lies necessarily below the one belonging to B_{2g}. Finally the $\pi_{z,+}$ combination will have negligibly small interactions with lower lying σ-orbitals. The resulting reorganization of the orbital scheme after through-bond interaction is shown qualitatively in Figure 5 ('th. bd.').

For obvious reasons it is rather difficult to assess empirically the size of the two postulated effects. Assuming that $6b_{1u}(\pi)$ is completely devoid of through-bond interaction, that the orbital energy of $\pi_{x,+}$ (*i.e.* through-space interaction only!) lies only little below that of $2b_{3u}(\pi)$ (say 0 to -0.5 eV) and that the ratio of the through-space interaction is indeed governed by $S_\sigma/S_\pi = 4.61$, one finds that the relevant cross-terms are $\langle \pi_{z,1} | \mathcal{H} | \pi_{z,5} \rangle = +0.6_5$ to $+1.0_5$ eV and $\langle \pi_{x,1} | \mathcal{H} | \pi_{x,5} \rangle = -0.1_5$ to -0.2_0 eV. (The positive sign in the former is a consequence of the phase

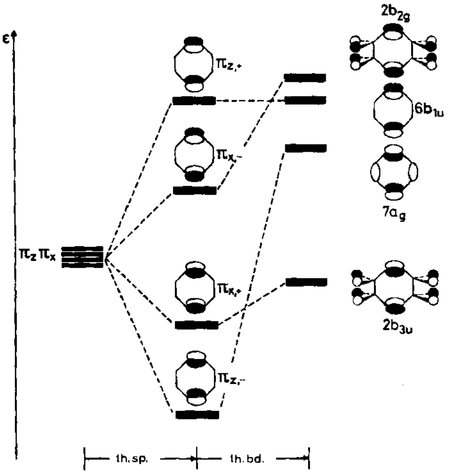


Fig. 5. *Qualitative diagram for the interplay of 'through-space' and 'through-bond' interactions of the basis π-orbitals in* **2**

definition for the basis functions). This moves the basis energies $\alpha(\pi)$ to -9.9_5 to -10.3_5 eV. In view of the observed shift by −2.1 eV of the onset of the σ-band system in going from 1 to 2, such a low value for $\alpha(\pi)$ is not unreasonable. Note however, that all these quantities refer to a very crude LCBO-model.

Table 4. *Analysis of the through-space and through-bond interaction in 1,5-cyclooctadiyne* (**2**) *by applying the* Edmiston-Ruedenberg *localization procedure to the* SPINDO and MINDO/2 *canonical SCF orbitals*

	(a)	(b)	(c)	(d)	(e)	(f)	(g)
	ψ_j	$\varepsilon(\psi_j)$	ρ_j	$\varepsilon(\rho_j)$	$\langle\rho_j\vert\psi_j\rangle^2$	$1-\langle\rho_j\vert\psi_j\rangle^2$	$\varepsilon(\psi_j)-\varepsilon(\rho_j)$
SPINDO	$2b_{2g}(\pi)$	-10.04	$\pi_{x,-}$	-10.77	0.80	0.20	0.73
	$6b_{1u}(\pi)$	-10.29	$\pi_{z,+}$	-10.72	0.95	0.05	0.43
	$7a_g(\pi)$	-10.32	$\pi_{z,-}$	-12.24	0.69	0.31	1.92
	$2b_{3u}(\pi)$	-10.37	$\pi_{x,+}$	-10.99	0.89	0.11	0.62
MINDO/2	$2b_{2g}(\pi)$	- 9.20	$\pi_{x,-}$	-10.64	0.61	0.39	1.44
	$6b_{1u}(\pi)$	- 9.33	$\pi_{z,+}$	- 9.68	0.72	0.28	0.35
	$7a_g(\pi)$	- 9.50	$\pi_{z,-}$	-12.32	0.55	0.45	2.82
	$2b_{3u}(\pi)$	-10.14	$\pi_{x,+}$	-11.22	0.83	0.17	1.08

[a] Canonical π-orbitals ψ_j; [b] Orbital energies (in eV) of the canonical π-orbitals ψ_j; [c] Symmetry adapted localized orbitals ϱ_j (see (7), where $\pi_{x,\mu}$ and $\pi_{z,\mu}$ now stand for localized π-orbitals); [d] Orbital energies (in eV) of the symmetry adapted localized orbitals ϱ_j; [e] Squared overlap between ψ_j and ϱ_j, yielding the π-character of the canonical orbital ψ_j; [f] σ-Character of the canonical orbital ψ_j; [g] Difference between the orbital energies of the canonical orbitals ψ_j and the symmetry adapted localized orbitals ϱ_j, which measures the degree of through-bond σ, π-interaction.

These conclusions are supported by a more detailed analysis of the MINDO/2 and SPINDO calculations summarized in Table 3. If the canonical orbitals ψ_j of **2** are subjected to an *Edmiston-Ruedenberg* localization procedure [18] one obtains localized $\pi_{x,1}$, $\pi_{x,5}$, $\pi_{z,1}$, $\pi_{z,5}$ orbitals, which exhibit the following characteristics: orbital energies $\alpha(\pi_{x,1}) = \alpha(\pi_{x,5})$, −10.88 eV (SPINDO), −10.93 eV (MINDO/2), $\alpha(\pi_{z,1}) = \alpha(\pi_{z,5})$, −11.48 eV (SPINDO), −11.00 eV (MINDO/2); coefficients $|c_i|$ of the 2s, $2p_x$, $2p_y$, $2p_z$ atomic orbitals in $\pi_{x,1}$ and $\pi_{x,5}$: 0, 0.704, 0,0 (SPINDO), 0, 0.705, 0,0 (MINDO/2); in $\pi_{z,1}$ and $\pi_{z,5}$: 0.001, 0, 0.280, 0.636 (SPINDO), 0,0, 0.151, 0.686 (MINDO/2); degree of localization given by $2\Sigma c_i^2$ for $\pi_{x,1}$ and $\pi_{x,5}$: 0.992 (SPINDO), 0.994 (MINDO/2); for $\pi_{z,1}$ and $\pi_{z,5}$: 0.967 (SPINDO), 0.986 (MINDO/2). If these localized orbitals are combined according to (7) to form the symmetry-adapted linear combinations $\varrho_j = \pi_{x,-}, \pi_{x,+}, \pi_{z,-}, \pi_{z,+}$ underlying the canonical orbitals ψ_j, the results given in Table 4 and Figure 6 are obtained.

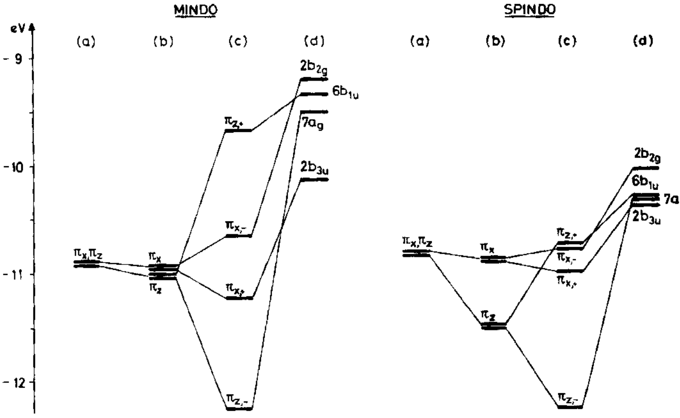


Fig. 6. *Orbital correlation diagrams for* SPINDO *and* MINDO/2 *models of 1,5-cyclooctadiyne* **2.** [a]) Localized orbitals for a linear C≡C bond; [b]) Localized orbitals for a *cis*-bent C≡C bond with $\theta = 20°$; [c]) Symmetry adapted semilocalized π-orbitals as given in (7) which incorporate the pure through-space interaction; [d]) Canonical orbitals which include through-bond interaction

As is evident from these data the same discrepancies as those observed previously in the case of a *cis*-bent dimethylacetylene are again present, in as far as the orbital energies $\alpha(\pi_{x,1})$ and $\alpha(\pi_{z,1})$ are practically degenerate in the MINDO/2 approximation whereas they are separated by 0.6 eV in the SPINDO model. On the other hand the cross terms between the pairs of localized $\pi_{x,1}$, $\pi_{x,5}$ and $\pi_{z,1}$, $\pi_{z,5}$ which can be considered as a measure of the through space interaction are $\langle \pi_{x,1} | \mathfrak{F} | \pi_{x,5} \rangle = -0.11$ eV (SPINDO), −0.29 eV (MINDO/2) and $\langle \pi_{z,1} | \mathfrak{F} | \pi_{z,5} \rangle = +0.76$ eV (SPINDO), +1.32 eV (MINDO/2) respectively. The absolute value of the ratio $+1.32/-0.29 = 4.55$ of the interaction terms obtained from the MINDO/2 procedure is identical to the ratio $S_\sigma/S_\pi = 4.61$ calculated above. In contrast the SPINDO model yields $+0.76/-0.11 = 6.91$, *i.e.* a somewhat larger value. In part, the reason is that the SPINDO procedure uses a *Slater* exponent of 1.925 for carbon.

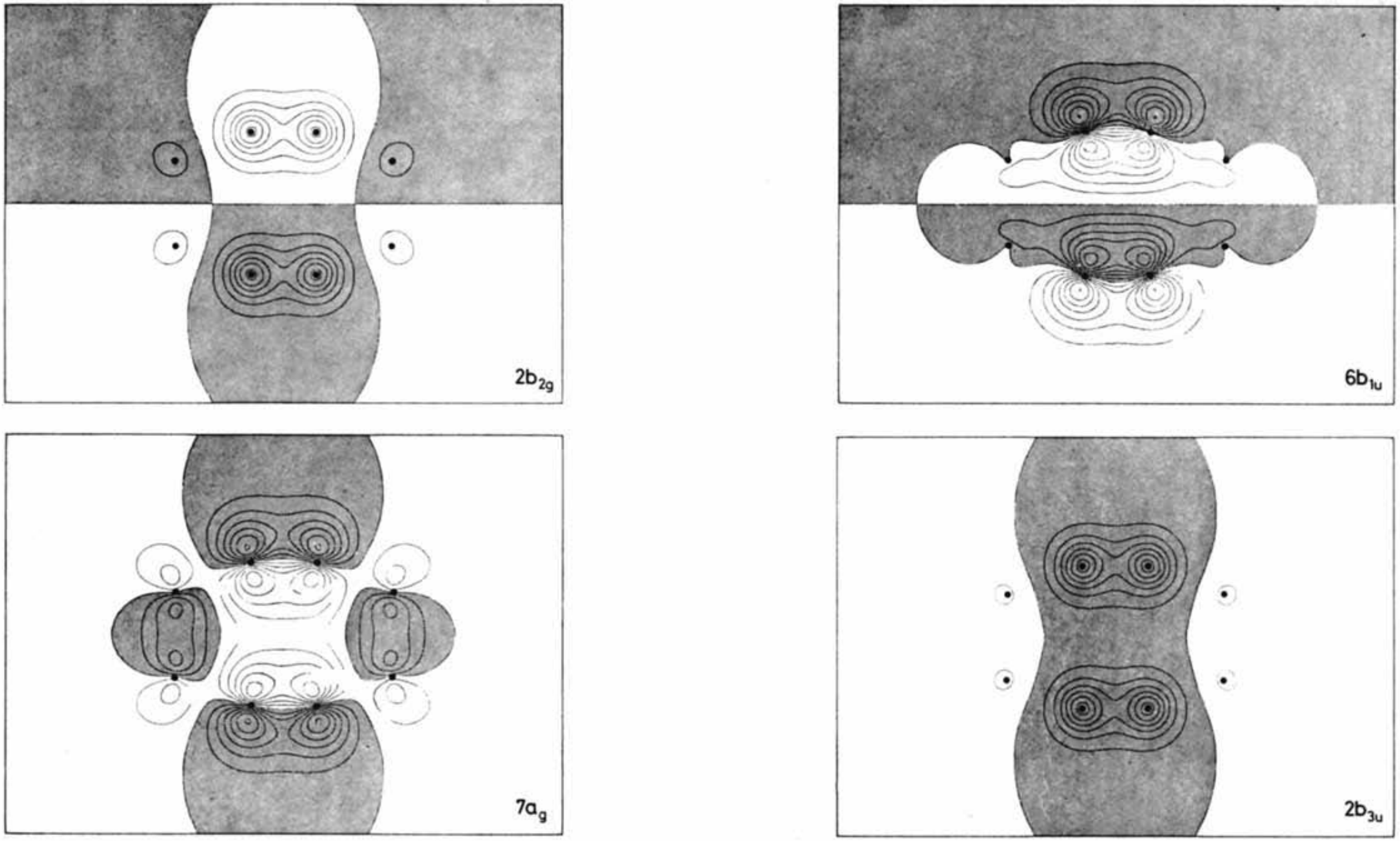


Fig. 7. *Contour maps of the canonical π-orbitals of 1,5-cyclooctadiyne* (**2**). The contours differ by 0.1 $(e/Å^3)^{1/2}$. The sections through the canonical orbitals are the y, z plane containing the carbon nuclei for orbitals 6b$_{1u}$ and 7a$_g$, and a plane parallel to the former but 0.28 Å above it for 2b$_{2g}$ and 2b$_{3u}$

From the overlap integrals $\langle \varrho_j \mid \psi_j \rangle$ between the symmetry adapted semilocalized linear combinations ϱ_j with the corresponding canonical orbitals ψ_j, as well as from the energy differences $\varepsilon(\psi_j) - \varepsilon(\varrho_j)$ given in Table 4, which measure the through bond interaction between $\pi_{x,1}$ and $\pi_{x,5}$ or $\pi_{z,1}$ and $\pi_{z,5}$, it becomes obvious that the two models used in this analysis differ seriously in their assessment of this effect. Therefore their agreement with respect to the ordering of the π-orbitals in **2** is presumably accidental. This is particularly evident from the diagrams given in Figure 6.

In Figure 7 are shown orbital plots for the four highest occupied canonical π-orbitals ψ_j of **2**, based on the results of the SPINDO calculations. For $6b_{1u}(\pi)$ and $7a_g(\pi)$ the intersecting plane coincides with the y, z plane of the molecule, for $2b_{2g}(\pi)$ and $2b_{3u}(\pi)$ it passes 0.28Å above this plane (which is a nodal plane in these two latter cases). The lines of constant ψ_j-value are spaced by 0.1 $(e/\text{Å}^3)^{1/2}$. Shaded and non-shaded areas correspond to opposite phases of ψ_j.

The two orbitals $2b_{2g}(\pi)$ and $2b_{3u}(\pi)$ show the expected behaviour, inasmuch as they correspond in essence to the pure linear combinations $\pi_{x,-}$ and $\pi_{x,+}$ defined in (7), interacting with the methylene pseudo π-orbitals. It should be noted that in the diagrams the evidence for this type of mixing is only slight, because SPINDO definitely underestimates such contributions (see also Tab. 4). The contour diagrams for $6b_{1u}(\pi)$ and $7a_g(\pi)$ are more revealing. It is seen that the $\pi_{z,1}$ and $\pi_{z,5}$ orbitals bulge outwards, thus relieving the electron-electron repulsion in the centre of the ring. Although the in-plane localized π-orbitals $\pi_{z,1}$ and $\pi_{z,5}$ are devoid of 2s-character (see above), 2s is mixed into the canonical orbitals through interaction of $\pi_{z,1}$ and $\pi_{z,5}$ with the localized CC-σ and CH_2-σ orbitals. The balance of these effects is obviously such that electron ejection from the orbital $6b_{1u}(\pi)$, which suffers only a minor amount of through bond contribution from the CC-σ bonds in positions 3,4 and 7,8, yields a band at 9.30eV, *i.e.* at the same position as the π-band in diethylacetylene **7** (9.25 eV) [9].

The sizeable through-bond CC-σ contribution, evident from the contour-diagram of orbital $7a_g(\pi)$, is responsible for the large destabilization by ~1.9 eV (SPINDO) or ~2.8 eV (MINDO/2) relative to the energy of the linear combination $\pi_{z,-}$ (see (7) and Tab. 4). The situation is reminiscent of the one prevailing in [2,2]paracyclophane (**6**) [23] where it has been shown [24] that the through-bond interaction destabilizes the $B_{3u}(\pi)$-linear combination of the benzene π-orbitals by about 1.5 eV. Assuming in a crude approximation that the through-bond interaction is proportional to the π-orbital coefficients in positions 1,2,5,6 of **2** and 3,6,11,14 of **6**, we expect a ratio of $(1/\sqrt{2})/(1/\sqrt{3}) = 1.23$ (for the relative through-bond destabilizations). This leads to an expectation value of $1.23 \cdot 1.5\,\text{eV} = 1.9\,\text{eV}$ for the upward through-bond shift of the $7a_g(\pi)$ orbital energy, in qualitative agreement with the observed pattern sketched in Fig. 5.

1,6-dithiacyclodeca-3,8-diyne (3). – As mentioned above, the two acetylene moieties of this molecule are practically linear and separated by more than 3Å. The overlap integrals S_π and S_σ between the carbon 2p AOs in positions 3,9 or 4,8 (*Slater* exponent 1.625) are $S_\pi = 0.0096$ to 0.0048 and $S_\sigma = 0.0555$ to 0.0321 for $R = 3$Å to 3.3Å, leading to a ratio S_σ/S_π of 5.79 to 6.67. From those values we deduce that the through space interaction between the $\pi_{xy,3}$ and $\pi_{xy,8}$ orbitals and the $\pi_{z,3}$ and $\pi_{z,8}$ orbitals of **3** is respectively 2.6 to 5.2 or 2.0 to 3.5 times smaller than in **2**. Using the empirical parameters for through-space interaction in **2** derived above, we get, as a first guess $\langle \pi_{xy,3} \mid \mathcal{H} \mid \pi_{xy,8} \rangle < -0.1$ eV and $\langle \pi_{z,3} \mid \mathcal{H} \mid \pi_{z,8} \rangle \approx 0.3$ to 0.6 eV.

On this basis we would expect that the split between the symmetry adapted linear combinations of the $\pi_{xy,3}$ and $\pi_{xy,8}$ orbitals is vanishingly small ($<.2$ eV), whereas the one between those of $\pi_{z,3}$ and $\pi_{z,8}$ should be of the order of $\sim$0.6 to 1.2 eV, if we disregard through-bond interactions. Assuming that the orbital energy of these basis π-orbitals is roughly that observed for dimethylacetylene [25] *i.e.* -9.6 eV, we would expect π-bands in the PE. spectrum of **3** near the following values: single band at $\sim$9.1 eV, double band at $\sim$9.6 eV and a single band at $\sim$10.1 eV.

A complicating feature is the presence in **3** of the sulfur 3p lone pair orbitals. Ejection of an electron from such orbitals in mercaptanes RSH and disulfides RSSR gives rise to PE. bands in the following positions (all values in eV): RSH 9.44 (R = methyl), 9.29 (R = ethyl), 9.19 (R = *n*-propyl) [26]; RSSR 8.67 (R = methyl), 8.44 (R = ethyl), 8.34 (R = *n*-propyl) [27]. In **4** the sulfur lone-pair band has been observed at 8.19 eV [4]. Introducing a double bond in positions 2,3 of *n*-PrSH, yielding $CH_2{=}CH{-}CH_2SH$, shifts the lone-pair band to 9.25 eV [28]. A similar, albeit slightly larger shift is observed in going from tetrahydrothiophene (8.40 eV) to 2,5-dihydrothiophene (8.54 eV) [29]. These data suggest that the energy of the basis 3p sulfur lone pair orbitals in **3** should lie near -9 eV, *i.e.* an energy close to that of the out-of-phase π_z-linear combination belonging to the irreducible representation A_u. Whereas in 1,4-dithiane a split of 0.5 eV is observed between the symmetric and antisymmetric linear combination of the 3p lone pair orbitals, as a consequence of through-bond interaction [30], the large distance between these orbitals in **3** leads us to expect almost zero split. Consequently, the two accidentally degenerate linear combinations $n_+ = (3p_1 + 3p_6)/\sqrt{2}$ and $n = (3p_1 - 3p_6)/\sqrt{2}$ will coincide in energy with the highest occupied π-orbital, leading to a first PE. band containing three strongly overlapping components. This is indeed what is observed, inasmuch as the first three features in the PE. spectrum of **3** exhibit an intensity ratio of 3:2:1, corresponding to ionization process from $(14a_g(n_-); 13b_u(n_+); 9a_u(\pi_{z,+}))$, $(8b_g(\pi_{xy,-});$

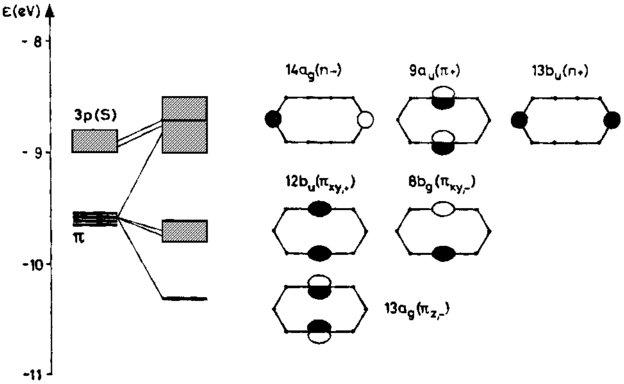


Fig. 8. *Orbital diagram for the six highest occupied orbitals of 1,6-dithiacyclodeca-3,8-diyne* (**3**)

$12b_u(\pi_{xy,+})$), ($13a_g(\pi_{z,-})$). Note that the orbital sequence inside the first two brackets is arbitrary. The indices + and – refer to the linear combinations as defined in analogy to (7) and to the lone pair combinations relative to parallel oriented $3p_1$ and $3p_6$ sulfur AOs (see Fig. 8).

In order to prove this assignment we have made use of the fact that 3p and 2p orbitals show different PE. cross sections as a function of excitation energy [31], *e.g.* for HeI (21.2 eV) and HeII (40.8 eV) radiation. Figure 3 shows the PE. spectrum of **3** recorded under HeII excitation. As can be seen the first band system at 9 eV is strongly reduced in intensity relative to the recording with HeI radiation, thus proving our assumption that this feature contains the two bands due to ejection from the lone-pair orbitals $14a_g(n_+)$ and $13b_u(n_-)$.

An EHT treatment [12] of **3** using the standard parameters and the experimental C_{2h} structure data, yields the following orbital sequence (orbital energies in eV): $14a_g(n_-)$, –12.06; $9a_u(\pi_{z,+})$, –12.32; $13b_u(n_+)$, –12.50; $12b_u(\pi_{xy,+})$, –12.85; $8b_g(\pi_{xy,-})$, –12.95; $13a_g(\pi_{z,-})$, –13.36. This is in excellent agreement with the observed band pattern (relative spacings within and between the first three prominent features), as can be seen by shifting the calculated orbital energies uniformly by 3.4 eV. This assignment is summarized in Figure 8.

Concluding remarks. – For the title compound **2** the observed π-band positions, an empirical estimate of the relative sizes of through-space and through-bond interactions and semiempirical molecular orbital calculations suggest the following assignment:

Band:	①	②	③	④	(8)
Orbital:	$2b_{2g}(\pi)$	$6b_{1u}(\pi)$	$7a_g(\pi)$	$2b_{3u}(\pi)$	

The first three bands overlap strongly whereas the fourth stands isolated. From Figure 5 and especially from the orbital diagrams given in Figure 7 we expect that electron ejection from orbital $2b_{3u}(\pi)$, which shows the least σ-π-mixing of the four π-orbitals and is thus almost pure π, will lead to a PE. band with dominating $0 \leftarrow 0$ vibrational component. On the other hand the orbital $7a_g(\pi)$ is very strongly mixed and as a consequence the PE. band correlated with an electron removal from it should be broad, the vertical ionization process (1) being associated with higher components of a complicated vibrational fine structure. The two remaining bands should exhibit an intermediate *Franck-Condon* envelope, which however, must be rather narrow, because of the limited σ-π-mixing present in $2b_{2g}(\pi)$ and $6b_{1u}(\pi)$. These predicted band shapes agree rather well with the observed ones, if the sequence (8) is accepted. As can be seen band ④ is very sharp, ③ must be rather broad and the two overlapping bands ①, ② are intermediate.

The PE. spectrum of **2** can only be understood if both through-space and through-bond interactions are taken explicitely into consideration and if they are of comparable magnitude. In addition one has to assume that the pronounced deviation of the C–C≡C–C moieties from collinearity does not discriminate between the basis energies $\alpha(\pi_z)$ and $\alpha(\pi_x)$ of the out-of-plane and in-plane π-orbitals.

Because of the larger separation between the triple bonds in **3**, the observed PE. spectrum is easier to interpret. Apart from hyperconjugation of the π-orbitals with the adjacent methylene groups, only through-space interaction needs to be invoked between the in-plane π-orbitals $\pi_{z,3}$ and $\pi_{z,8}$.

An important feature underlying both assignments is, that the energy of the basis π-orbitals is rather insensitive to *cis*-bending, if $\theta < 20°$ (see (4)). As has been demonstrated convincingly by *Schmidt, Schweig* & *Krebs* [4] the accidental degeneracy is only lifted significantly if $\theta > 20°$.

It is of course not possible to infer in a straightforward manner from the PE. spectra how such a departure from collinearity will affect other physico-chemical properties of these molecules, *e.g.* Δ Hh the enthalpy of hydrogenation. Unfortunately only an unreliable value of $\Delta \mathrm{Hh} = -69$ kcal mol^{-1} is available for **1** [32], to be compared to $\Delta \mathrm{Hh} = -62.8$ kcal mol^{-1} for octyne-4 or $\Delta \mathrm{Hh} = -61.9$ kcal mol^{-1} for cyclononyne. A more detailed investigation of Δ Hh, including **2**, is under way [33].

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REFERENCES

[1] *C. Batich, O. Ermer, E. Heilbronner & J. R. Wiseman*, Angew. Chem. *85*, 302 (1973); Int. Ed. *12*, 312 (1973).

[2] *E. Kloster-Jensen & J. Wirz*, Angew. Chem. *85*, 723 (1973); Int. Ed. *12*, 671 (1973).

[3] *G. Eglinton, I. A. Lardy, R. A. Raphael & G. A. Sim*, J. Chem. Soc. *1964*, 1154.

[4] *A. Krebs & H. Kimling*, Tetrahedron Letters *1970*, 761; Nachr. Chem. Techn. *19*, 272 (1971); *A. Krebs & H. Kimling*, Angew. Chem. *83*, 540 (1971); *H. Schmidt, A. Schweig & A. Krebs*, Tetrahedron Letters *1974*, 1471.

[5] *J. Haase & A. Krebs*, Z. Naturforsch. *26a*, 1190 (1971).

[6] *Ch. Römming*, private communication; cf. ref. [2].

[7] *H. Hope, J. Bernstein & K. Trueblood*, Acta Crystallogr. *B28*, 1733 (1972).

[8] *D. W. Turner*, Proc. Roy. Soc. (London) *A307*, 15 (1968).

[9] *E. Heilbronner & V. Hornung*, unpublished results.

[10] *D. W. Turner, C. Baker, A. D. Baker & C. R. Brundle*, 'Molecular Photoelectron Spectroscopy', Wiley-Interscience, London, p. 170.

[11] *R. Hoffmann, A. Imamura & W. J. Hehre*, J. Amer. chem. Soc. *90*, 1499 (1968).

[12] *R. Hoffmann*, J. chem. Physics *39*, 1397 (1963); *R. Hoffmann & W. N. Lipscomb, ibid. 36*, 2179, 3489 (1962); *ibid. 37*, 2872 (1962).

[13] *M. J. S. Dewar & E. Haselbach*, J. Amer. chem. Soc. *92*, 590 (1970); *I. Bodor, M. J. S. Dewar, A. Harget & E. Haselbach, ibid. 92*, 3854 (1970); *G. Klopman & B. O'Leary*, Fortschr. chem. Forsch. *15*, 445 (1970).

[14] *E. Haselbach*, Helv. *54*, 1981 (1971).

[15] *B. M. Gimarc*, J. Amer. chem. Soc. *92*, 266 (1969).

[16] *P. Millie, L. Praud & J. Serre*, Int. J. Quantum Chem. *4*, 187 (1971).

[17] *C. Fridh, L. Asbrink & E. Lindholm*, Chem. Physics Letters, *15*, 282 (1972); *L. Asbrink, C. Fridh & E. Lindholm*, J. Amer. chem. Soc. *94*, 5501 (1972).

[18] *C. Edmiston & K. Ruedenberg*, Rev. Mod. Physics *35*, 457 (1963); *J. Chem. Physics 43*, 597 (1965); *W. England, L. S. Salmon & K. Ruedenberg*, Fortschr. chem. Forsch. *23*, 31 (1971); *C. Trindle & O. Sinanoglu*, J. chem. Physics *49*, 65 (1968).

[19] *L. Radom, J. A. Pople & W. L. Mock*, Tetrahedron Letters *1972*, 479; *W. L. Mock, ibid. 1972*, 475.

[20] *R. Hoffmann*, Accounts of Chem. Res. *4*, 1 (1971).
[21] *C. Batich, P. Bischof & E. Heilbronner*, J. Electron Spectrosc. *1*, 333 (1972/73).
[22] *R. C. Sahni & J. W. Cooley*, Technical Note D-146-I, NASA, Washington, 1959.
[23] *R. Boschi & W. Schmidt*, Angew. Chem. *83*, 408 (1973); Int. Ed. *12*, 402 (1973).
[24] *E. Heilbronner & J. P. Maier*, Helv. *57*, 151 (1974); *R. Gleiter*, Tetrahedron Letters *1969*, 4453.
[25] *C. Baker & D. W. Turner*, Proc. Roy. Soc. (London) *A 308*, 19 (1968); *F. Brogli, E. Heilbronner, V. Hornung & E. Kloster-Jensen*, Helv. *56*, 2171 (1973).
[26] *H. Ogata, H. Onizuka, Y. Nihei & H. Kamada*, Bull. chem. Soc. Japan *46*, 3036 (1973).
[27] *G. Wagner & H. Bock*, Chem. Ber. *107*, 68 (1974).
[28] *A. Katrib & J. W. Rabalais*, J. phys. Chemistry *77*, 2358 (1973).
[29] *H. Schmidt & A. Schweig*, Tetrahedron Letters *1973*, 1437.
[30] *D. A. Sweigart & D. W. Turner*, J. Amer. chem. Soc. *94*, 5599 (1972); *J. Daintith, R. Dinsdale, J. P. Maier, D. A. Sweigart & D. W. Turner*, in 'Molecular Spectroscopy 1971', The Institute of Petroleum, London, p. 16; *H. Bock & G. Wagner*, Angew. Chem. *84*, 119 (1972).
[31] *W. C. Price, A. W. Potts & D. G. Streets*, in: 'Electron Spectroscopy', Ed. *D. A. Shirley*, North-Holland Publishing Comp., Amsterdam, 1970, p. 187; *M. B. Robin, N. A. Kuebler & C. R. Brundle, ibid.*, p. 351; *A. Katrib, T. P. Debies, R. J. Colton, T. H. Lee & J. W. Rabalais*, Chem. Physics Letters *22*, 196 (1973); *A. Schweig & W. Thiel*, Mol. Physics *27*, 265 (1974); and references given therein.
[32] *R. B. Turner, A. D. Jarrett, P. Goebel & B. J. Mallon*, J. Amer. chem. Soc. *95*, 790 (1973).
[33] *A. Krebs*, private communication.
[34] *H. D. Martin & R. Schwesinger*, Chem. Ber., in print.

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143. Primary Photophysical and Photochemical Processes in the Photoreduction of a Naphthoquinone methide: 2-Phenylnaphtho[1,8-*bc*]furan-5-one

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(3. IV. 74)

Summary. The photochemical reactivity of the title compound **3** was studied in the context of a novel acid catalysed photocyclisation reaction recently discovered by *Barton et al.* [1b]. The following results were obtained by flash photolysis methods and steady state irradiations in the presence and absence of quenchers and sensitisers combined with luminescence measurements: The fluorescence of **3** in benzene is very weak and short-lived ($\phi_{Fl} \leq 10^{-4}$, $\tau_{Fl} \leq 10^{-9}$ s) due to efficient intersystem crossing ($\phi_T = 0.8 \pm 0.15$). On the other hand, the conjugate acid **4** exhibits an intense green fluorescence ($\phi_{Fl} = 0.9_7 \pm 0.1$) with a lifetime of $(4. \pm 1.) \cdot 10^{-9}$ s. Acidity constants of **4** in the ground and first excited triplet state were estimated in acetic/trifluoroacetic acid mixtures by comparison with *Hammett* indicators: $pK(S_0) = -0.3$, $pK(T_1) = +1$.

The *Förster* cycle yields $pK(S_1) = +6$, however, adiabatic protonation of S_1 (**3**) to produce fluorescent **4** is not efficient. The lowest $\pi\pi^*$ triplet state of **3** ($E_T = 45 \pm 1$ kcal/mol, $^3\tau = 8 \cdot 10^{-4}$s in dilute, degassed benzene solution) is an intermediate in the photoreduction of **3** by oxidisable substrates. Hydrogen abstraction from 2-propanol by T_1 (**3**) yields the semiquinone methide radical **5** which dimerises to **6**. On readmission of air after irradiation, **6** is reoxidised to the starting material **3**. Predictions derived from PPP SCF CI calculations are in accord with the observed spectroscopic and photochemical properties of **3**.