

are no significant differences between bond lengths and angles in the two molecules (*A* and *B*). The average out-of-plane distances for the 13 ring atoms in the two molecules are 0.022 and 0.029 Å respectively. Bond lengths in the indole regions of (I) and harmaline (III) (7-methoxy-3,4-dihydroharmalin, Reimers, Guth & Wang, 1984) are quite similar with the exception of C(4a)–C(4b) [1.45 (1) in (I), 1.409 (7) Å in (II)]. Hydrogen bonding links the molecules together in spiral chains along the *z* direction of the unit cell (Fig. 1). The N...H distances are 1.88 and 1.92 Å respectively. (II) shows similar hydrogen-bonding links.

This work was supported by the Foreign Relations Coordination Unit of the Supreme Council of Universities of Egypt (grant No. 831003), and through the facilities of the University of Maryland's Computer Science Center.

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Structures and Quantum-Mechanical Calculations of Two Polarized Nitroethylenes: C₉H₉ClN₂O₂S (I) and C₆H₁₃N₃O₂ (II)

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(Received 16 December 1985; accepted 21 April 1986)

Abstract. (I) 1-(*o*-Chloroanilino)-1-methylthio-2-nitroethylene, $M_r = 244.70$, monoclinic, $P2_1/c$, $Z = 4$, $a = 11.135$ (3), $b = 9.563$ (2), $c = 10.291$ (3) Å, $\beta = 101.69$ (6)°, $V = 1073.1$ (5) Å³, $D_x = 1.514$ g cm⁻³, $D_m = 1.51$ g cm⁻³ (by flotation), $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 5.21$ cm⁻¹, $F(000) = 504$, $T = 293$ K, $R = 0.0311$ (1147 observed reflections). (II) 1,1-Bis(dimethylamino)-2-nitroethylene, $M_r = 159.19$, monoclinic, $P2_1/n$, $Z = 4$, $a = 5.281$ (1), $b = 13.939$ (2), $c = 11.510$ (2) Å, $\beta = 98.74$ (3)°, $V = 837.4$ (3) Å³, $D_x = 1.263$ g cm⁻³, $D_m = 1.25$ g cm⁻³ (by flotation), $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.90$ cm⁻¹, $F(000) = 344$, $T = 293$ K, $R = 0.0621$ (913 observed reflections). The C=C bond lengths are 1.375 (4) Å in (I) and 1.406 (5) Å in (II) with extensive π delocalization in

both molecules. The ethylenic moiety is significantly twisted in (II), while it is almost exactly planar in (I) where an intramolecular H bond between the aminic nitrogen and the nitro group is present. Semiempirical quantum-mechanical calculations have also been carried out on the title compounds and on related molecules to estimate charge densities and bond orders as well as the preferred geometries.

Introduction. Polarized 1,1-XY-disubstituted 2-nitroethylenes, with *X* and/or *Y* an electron-donating group, have been extensively investigated. They can be described as push-pull ethylenes, a class of compounds presenting an unusually low rotational barrier around the C=C double bond (Isaakson, Sandström &

Wennerbeck, 1967) and an absorption in the near-ultraviolet region due to the delocalization of π electrons (Wennerbeck, 1973). Nitroethylenes are reactive and versatile intermediates in a number of organic syntheses (Gompper & Schaefer, 1967) of industrial interest, e.g. in the preparation of antiulcer agents (Allen & Hanburys Ltd, 1978; Martin-Smith, Price, Bradshaw & Cliterow, 1979) and of insecticidal, fungicidal, bactericidal and herbicidal products (Vishnu, 1980).

Recent calorimetric studies (DTA/DSC) performed in our laboratories evidenced the high instability of these compounds even at low temperature (exothermic decomposition at $T \leq 473$ K) and the related potential hazards in industrial manufacturing (Gronchi, Cardillo, Di Renzo & Del Rosso, 1982). In this work we report the results of a crystallographic and quantum-mechanical study of the title compounds carried out to correlate reactivity and spectroscopic data with structural parameters.

Experimental. Pale yellow single crystals of (I) and (II) (Allen & Hanburys Ltd, 1978; French, Peseke, Kristen & Bräuniger, 1976) with prismatic habit from ethyl acetate solutions, mounted on a glass fiber in a general orientation and used for all the analyses. Crystal dimensions and data collection procedures in Table 1. Direct methods, full-matrix refinement [function minimized $\sum w(|F_o| - |F_c|)^2$, weighting scheme in Table 1] with no absorption correction, anisotropic thermal parameters, H atoms located on a Fourier difference map and held fixed with thermal factors differentiated for each group. Largest Δ/σ 0.39 (scale factor) in (I) and 0.27 [U_{22} for C(1)] in (II), highest residual peak $0.17 \text{ e } \text{\AA}^{-3}$ in (I) and $0.21 \text{ e } \text{\AA}^{-3}$ in (II). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Solution and refinement with *SHELX76* (Sheldrick, 1976), geometrical calculations with *PARST* (Nardelli, 1982), thermal-motion analysis with *THMI* (Schomaker & Trueblood, 1968), semiempirical quantum-mechanical calculations with *CNDO/2* (Pople & Beveridge, 1970) and *MINDO/3* (Bingham, Dewar & Lo, 1975). For *CNDO/2* the experimental geometries corrected for thermal motion were used as input without any further refinement.

Discussion. Final atomic coordinates are given in Table 2, bond lengths and angles are reported in Table 3, while some selected torsion angles are given in Table 4.*

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, thermal motion analysis results and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 43012 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

An *ORTEP* (Johnson, 1976) view of the two compounds is shown in Figs. 1 and 2 and the packing diagram of compound (I) (see later) is given in Fig. 3. Residual charges and bond indices calculated from *CNDO/2* results (Mulliken, 1955; Wiberg, 1968) are in Fig. 4.

Both molecules show an extensive π delocalization involving the aminic nitrogen(s) and the nitroethylenic group. This system is however essentially planar in (I), while it is twisted in (II) due to steric interactions (see below), as best described by the two torsion angles $\text{N}(1)-\text{C}(1)-\text{C}(2)-\text{N}(2)$ and $\text{N}(1)-\text{C}(1)-\text{C}(2)-\text{N}(3)$ [-34.3 (5) $^\circ$ and 148.2 (3) $^\circ$ respectively, see Table 4]. The phenyl in (I) is not involved in the aforementioned conjugation, the dihedral angle between the phenyl plane and that defined by the rest of the molecule being 86.86 (8) $^\circ$. The extent of the conjugation and the

Table 1. *Data collection parameters*

	(I)	(II)
Diffractometer	PW 1100	PW 1100
Crystal dimensions (mm)	0.30 × 0.20 × 0.20	0.40 × 0.20 × 0.05
Reflections for cell constants	25 ($2\theta \geq 18^\circ$)	22 ($2\theta \geq 20^\circ$)
Scan speed ($^\circ \text{ s}^{-1}$)	0.03	0.03
Scan width ($^\circ$)	1.1	1.2
Total background count (s)	20	20
Scan mode	$\theta/2\theta$	$\theta/2\theta$
θ range ($^\circ$)	$6 \leq 2\theta \leq 48$	$5 \leq 2\theta \leq 50$
Maximum value of indices	± 12 10 11	± 6 16 13
Standard reflections	433, 433 and 433 (every 120 min)	122, 122 and 122 (every 90 min)
wR	0.0378	0.0667
S	0.70	1.63
Weighting scheme (optimized)	$k = 0.6951$	$k = 2.1398$
$w = k/(\sigma^2(F_o) + g F_o ^2)$	$g = 0.002337$	$g = 0.001009$
Independent measured reflections	1672	1470
Observation criteria [$I_{\text{net}}/\sigma(I)$]	2.5	2.0

Table 2. *Final atomic coordinates and equivalent isotropic thermal factors*

$$B_{\text{eq}} = \frac{8}{3}\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

Compound (I)	x	y	z	B_{eq}
S	0.23698 (7)	0.29999 (8)	0.45284 (9)	3.75 (4)
Cl	0.06196 (8)	0.04241 (10)	0.19282 (9)	4.90 (4)
C(1)	0.4109 (2)	0.2983 (3)	0.3011 (3)	3.2 (1)
C(2)	0.3316 (2)	0.2201 (3)	0.3579 (3)	2.9 (1)
C(3)	0.2414 (2)	-0.0032 (3)	0.4093 (3)	2.8 (1)
C(4)	0.1227 (2)	-0.0328 (3)	0.3460 (3)	3.1 (1)
C(5)	0.0490 (3)	-0.1208 (3)	0.4028 (3)	3.9 (2)
C(6)	0.0966 (3)	-0.1815 (3)	0.5239 (4)	4.2 (2)
C(7)	0.2156 (3)	-0.1536 (3)	0.5887 (3)	4.3 (2)
C(8)	0.2877 (3)	-0.0647 (3)	0.5308 (3)	3.8 (2)
C(9)	0.2733 (3)	0.4829 (3)	0.4463 (3)	4.3 (2)
N(1)	0.4860 (2)	0.2416 (2)	0.2242 (3)	3.5 (1)
N(2)	0.3204 (2)	0.0813 (2)	0.3471 (2)	3.2 (1)
O(1)	0.4875 (2)	0.1120 (2)	0.2038 (2)	3.8 (1)
O(2)	0.5533 (2)	0.3197 (2)	0.1737 (3)	5.1 (1)
Compound (II)				
C(1)	0.0698 (7)	0.5387 (2)	0.8517 (3)	3.0 (2)
C(2)	-0.0028 (6)	0.4500 (2)	0.7988 (3)	2.6 (2)
C(3)	-0.3771 (8)	0.5097 (3)	0.6680 (4)	4.6 (2)
C(4)	-0.1449 (9)	0.3689 (3)	0.6107 (4)	4.7 (2)
C(5)	0.3339 (7)	0.3691 (3)	0.9328 (4)	4.4 (2)
C(6)	-0.0512 (8)	0.2796 (3)	0.8485 (4)	4.1 (2)
N(1)	0.0903 (6)	0.6223 (2)	0.7913 (3)	3.4 (2)
N(2)	-0.1727 (6)	0.4411 (2)	0.7002 (2)	3.1 (1)
N(3)	0.0963 (6)	0.3692 (2)	0.8521 (2)	3.2 (1)
O(1)	0.0548 (5)	0.6253 (2)	0.6817 (2)	4.1 (1)
O(2)	0.1448 (6)	0.6975 (2)	0.8501 (3)	4.9 (2)

resulting polarization of the two molecules may be judged by the CNDO/2 results in Fig. 4: compound (II) shows about the same delocalization as (I), at least as judged from the values of C–N and N–O bonds, even in the presence of a significant twist around the C=C double bond which lowers the corresponding bond index in (II).

The C(1)–C(2) distances [1.375 (4) Å in (I) and 1.406 (5) Å in (II)*] are longer than the value of an isolated double bond [1.336 (2) Å for ethylene (Bartell, Roth, Hollowell, Kutchitsu & Young, 1965)], but are comparable to those found in aromatic systems and in other polarized ethylenes, such as 1.369 (7) Å for 1,1-bis(methylthio)-2-*p*-bromobenzoyl-2-cyanoethylene (Abrahamsson, Rehnberg, Liljefors & Sandström,

Table 3. Selected bond lengths (Å) and angles (°) including the values corrected for thermal motion

	(I)		(II)	
	Uncorrected	Corrected	Uncorrected	Corrected
C(1)–C(2)	1.375 (4)	1.378	1.406 (5)	1.412
C(1)–N(1)	1.374 (4)	1.378	1.369 (5)	1.375
C(1)–H(C1)	0.97	–	1.03	–
C(2)–N(2)	1.335 (4)	1.338	1.342 (4)	1.349
C(2)–N(3)	–	–	1.350 (4)	1.356
C(2)–S	1.751 (3)	1.756	–	–
S–C(9)	1.800 (3)	1.803	–	–
N(1)–O(1)	1.258 (3)	1.261	1.247 (4)	1.254
N(1)–O(2)	1.244 (4)	1.245	1.257 (4)	1.263
N(2)–C(3)	1.436 (4)	1.439	1.447 (5)	1.454
N(2)–C(4)	–	–	1.463 (5)	1.470
N(3)–C(5)	–	–	1.443 (5)	1.451
N(3)–C(6)	–	–	1.469 (5)	1.476
N(2)–H(N2)	1.07	–	–	–
C(4)–Cl	1.740 (3)	1.746	–	–
<C–C> _{av} ^{ph}	1.382 ± 0.003*	1.386 ± 0.002*	–	–
<C–H> _{av} ^{ph}	1.08 ± 0.03*	–	–	–
<C–H> _{av} ^{mc}	1.00 ± 0.04*	–	0.89 ± 0.11*	–
N(1)–C(1)–C(2)	123.3 (3)	–	124.5 (3)	–
N(1)–C(1)–H(C1)	115.8	–	117.1	–
C(2)–C(1)–H(C1)	120.3	–	117.8	–
C(1)–C(2)–S	120.7 (2)	–	–	–
C(1)–C(2)–N(2)	124.2 (3)	–	123.5 (3)	–
C(1)–C(2)–N(3)	–	–	118.4 (3)	–
S–C(2)–N(2)	115.1 (2)	–	–	–
N(2)–C(2)–N(3)	–	–	118.1 (3)	–
N(2)–C(3)–C(4)	121.3 (3)	–	–	–
N(2)–C(3)–C(8)	119.5 (3)	–	–	–
C(3)–C(4)–Cl	120.1 (2)	–	–	–
C(5)–C(4)–Cl	118.7 (2)	–	–	–
C(1)–N(1)–O(1)	121.0 (3)	–	122.0 (3)	–
C(1)–N(1)–O(2)	119.5 (3)	–	117.7 (3)	–
O(1)–N(1)–O(2)	119.5 (3)	–	120.3 (3)	–
C(2)–N(2)–H(N2)	123.1	–	–	–
C(3)–N(2)–H(N2)	111.4	–	–	–
C(2)–N(2)–C(3)	125.2 (2)	–	122.2 (3)	–
C(2)–N(2)–C(4)	–	–	122.2 (3)	–
C(3)–N(2)–C(4)	–	–	115.2 (3)	–
C(2)–N(3)–C(5)	–	–	122.2 (3)	–
C(2)–N(3)–C(6)	–	–	122.0 (3)	–
C(5)–N(3)–C(6)	–	–	115.0 (3)	–
C(2)–S–C(9)	103.8 (2)	–	–	–
<C–C–C> _{av} ^{ph}	120.0 ± 0.9*	–	–	–
<C–C–H> _{av} ^{ph}	120 ± 4*	–	–	–
<N–C–H> _{av} ^{mc}	–	–	113 ± 3*	–

* The ± sign refers to the standard deviation from the mean according to the expression $[\sum(x_i - \bar{X})^2 / (n-1)]^{1/2}$.

Table 4. Most relevant torsion angles (°) with e.s.d.'s on last digit in parentheses

	(I)	(II)
N(1)–C(1)–C(2)–N(2)	1.4 (5)	–34.3 (5)
N(1)–C(1)–C(2)–N(3)	–	148.2 (3)
N(1)–C(1)–C(2)–S	–179.1 (2)	–
O(1)–N(1)–C(1)–C(2)	–1.5 (4)	–2.9 (5)
O(2)–N(1)–C(1)–C(2)	178.4 (3)	176.6 (3)
C(2)–N(2)–C(3)–C(4)	90.6 (4)	–
C(2)–N(2)–C(3)–C(8)	–94.2 (4)	–
C(1)–C(2)–N(2)–C(3)	–	–28.6 (5)
C(1)–C(2)–N(2)–C(4)	–	143.3 (4)
C(1)–C(2)–N(3)–C(5)	–	–23.2 (5)
C(1)–C(2)–N(3)–C(6)	–	145.7 (3)

* For a more significant comparison with other crystallographic determinations, in the text we will use the bond lengths without thermal motion correction.

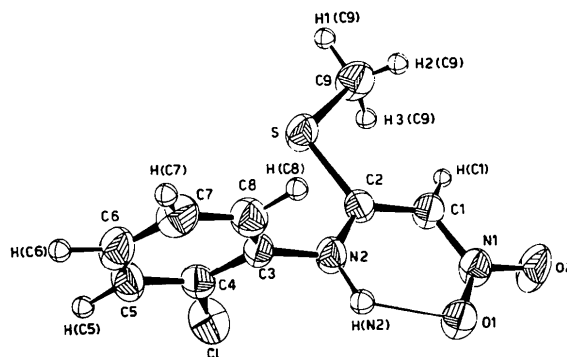


Fig. 1. An ORTEP view of compound (I).

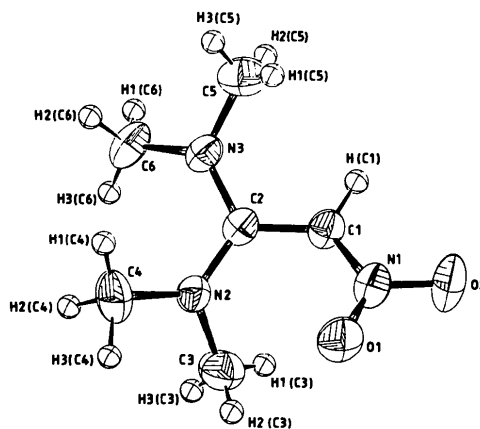


Fig. 2. An ORTEP view of compound (II).

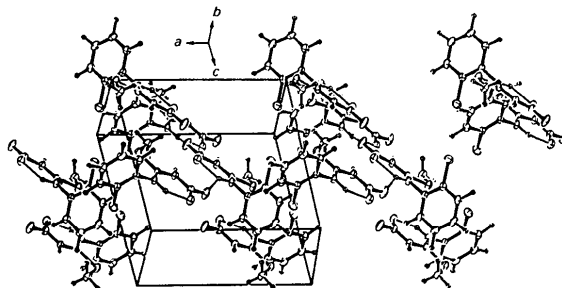


Fig. 3. The packing diagram of compound (I).

1974) or 1.409 (4) Å for 3-[bis(dimethylamino)-methylene]-3-phenyl-2-propanone (Kamath & Venkatesan, 1984). Moreover, the C—N bonds are significantly shortened: for the aminic nitrogens we found 1.335 (4) Å for C(2)—N(2) in (I) and 1.342 (4) Å for C(2)—N(2) (*cis* to the nitro group) and 1.350 (4) Å for C(2)—N(3) in (II). Similar bond lengths have been reported for 1,3-dimethyl-2-[(*p*-bromobenzoyl)cyanomethylene]imidazolidine [average value 1.328 (5) Å, Abrahamsson *et al.*, 1974]. The C(1)—N(1) distances involving the nitro group are slightly longer [1.374 (4) Å in (I) and 1.369 (5) Å in (II)], but still much less than 1.486 (12) Å for *trans*-1-(2-chloro-4-dimethylaminophenyl)-2-nitroethylene (Cameron, Cowley & Thompson, 1974), a value which is even larger than the 1.475 Å found in nitromethane (*International Tables for X-ray Crystallography*, 1962) or 1.470 Å in nitroethylene (Hess, Bauder & Günthard, 1967). A further indication of an efficient π conjugation is the lengthening of the N—O bonds (see the values in Table 3) with respect to the value of 1.218 Å in nitroethylene (Hess *et al.*, 1967) or the range of values [1.203 (5)—1.226 (5) Å] in 1,4-dinitrocyclooctatetraene (Furmanova & Struchkov, 1978). Finally, the difference in lengths between the two C—S bonds in (I) is consistent with that found in 1,1-bis(methylthio)ethylene (Jandal, Seip & Torgriksen, 1976) [1.767 (5) Å for C(sp^2)—S and 1.815 (5) Å for C(sp^3)—S as measured in the gas phase] and must be attributed only to the different hybridization of the two carbon atoms as discussed, *e.g.*, for *S*-methylidithione (Preuss & Gieren, 1975).

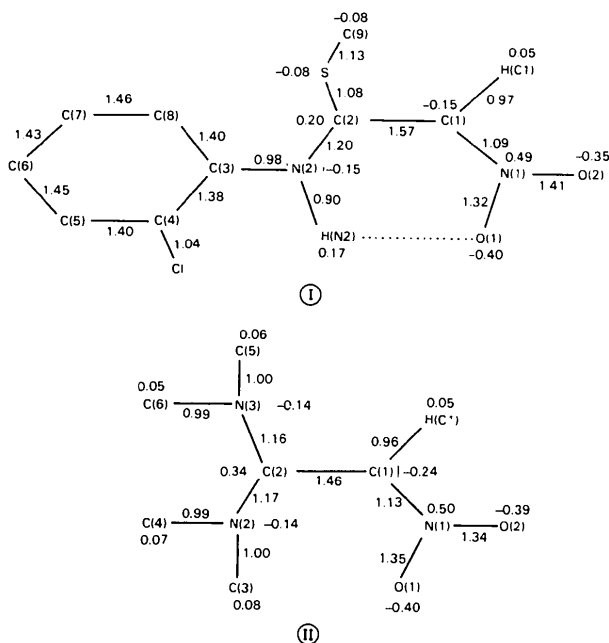
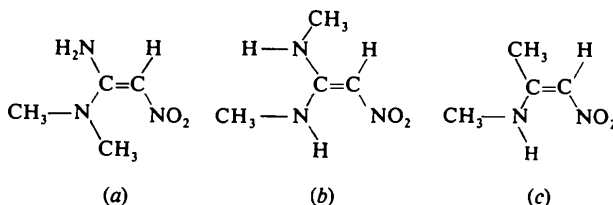


Fig. 4. Bond indices and residual charges calculated with CNDO/2.

In keeping with the extensive conjugation, in both compounds the aminic nitrogens are best described as sp^2 hybridized (see the relevant bond angles in Table 3 which further show the almost exact planarity of the aminic group). This is achieved in compound (II) notwithstanding a twist around the bonds C(2)—N(2) and C(2)—N(3) (see Table 4) so as to relieve the steric compression with the nitroethylenic part. As a result, the most relevant non-bonded interactions in compound (II) are C(1)···C(3) 2.947 (5) Å, C(1)···C(5) 2.831 (5) Å, C(4)···C(6) 2.978 (6) Å, O(1)···C(3) 2.777 (5) Å [with O(1)···H2(C3) 2.46 Å and O(1)···H2(C3)—C(3) 98.7° indicating possibly some form of hydrogen bonding] and O(1)···N(2) 2.856 (4) Å. On the other hand, in compound (I) there is a strong intramolecular hydrogen bond O(1)···H(N2) [1.93 Å, while O(1)···N(2) is 2.614 (4) Å and O(1)···H(N2)—N(2) is 117.9°] which gives a stable six-membered ring. This interaction may be responsible for lengthening the N(1)—O(1) bond compared with N(1)—O(2), although the difference is at the limit of statistical significance. Furthermore, an intermolecular hydrogen bond involves O(2) and H(N2)', related to the corresponding atom of the original set by the symmetry operation $1-x, \frac{1}{2}+y, \frac{1}{2}-z$ [2.04 Å for O(2)···H(N2)' and 2.899 (3) Å for O(2)···N(2)', with O(2)···H(N2)'—N(2)' 134.7°]; this results in a chain running approximately along the *b* axis.

A general feature of polarized push-pull ethylenes is the substantial lengthening of the C=C bond. This appears to be correlated with an unusually low activation free energy of rotation ΔG^\ddagger and a twist which may be exceptionally large (Adhikesavalu, Kamath & Venkatesan, 1983). If both electronic and steric effects undoubtedly play some role in the double-bond lengthening, the observed twist must be attributed in general to steric effects, being larger when double-bond substituents are bulkier. It is noteworthy that compound (I) departs from the general correlation between bond lengths and torsion angles (Adhikesavalu *et al.*, 1983), as does 3-(2-imidazolidinylidene)-2,4-pentanedione (Adhikesavalu & Venkatesan, 1983). In both compounds the lower steric interactions and the strong intramolecular hydrogen bond(s) are essential for the planarity of the two molecules. To test the relative weight of these two effects, we have carried out MINDO/3 calculations with geometry optimization on the related model compounds (a)–(c)



where (a) and (b) have two donor groups, while only (b) and (c) may form an intramolecular hydrogen bond. The geometry optimization results, in terms of the most relevant torsion angles, are reported in Table 5 for the three molecules. Refinements in which specific parts of compounds (a) and (b) were constrained to be planar have also been carried out.

Molecule (a) is the most crowded one, with heavy interference between an aminic CH₃ and the NO₂ group in the completely planar conformation. To relieve this interaction the fully optimized geometry shows a twist angle [column (a)1, Table 5] close to that found experimentally for compound (II). By imposing the planarity of C(1), C(2), N(1), N(2) and N(3) [column (a)2], the steric repulsion is avoided through an off-plane twist of the two oxygen atoms, but the computed energy is 3.5 kcal mol⁻¹* higher (1 kcal mol⁻¹ ≡ 4.2 kJ mol⁻¹). Forcing also the torsion angles involving the two oxygen atoms to have the experimental values [column (a)3], the resulting energy is even higher [5.0 kcal mol⁻¹ with respect to (a)1].

Complete optimization of compound (b) gives again a twisted molecule, although to a lesser extent than (a) [see column (b)1]. Imposing again the coplanarity constraint to atoms C(1), C(2), N(1), N(2) and N(3) [column (b)2, to be compared with (a)2] the lower steric requirements and the existence of the hydrogen bond allow an essentially planar geometry only 1.0 kcal mol⁻¹ less stable than the fully optimized (b)1. The precise amount of destabilization may be somewhat in error, because of the limited ability of MINDO/3 to evaluate the energy associated with hydrogen bonds (Dewar, Zoebish, Healy & Stewart, 1985).

Compound (c) is less polarized because of the presence of only one aminic donor group. This leads to a decreased conjugation and therefore to a higher C=C bond index in (c) as compared with (b): the corresponding computed values (Wiberg, 1968) are 1.490 for (c), 1.354 for (b)1 and 1.369 for (b)2, and if we assume that the σ contribution is essentially the same, the differences between these values roughly give the corresponding differences between the π contribution. [Note that in compound (I) the π contribution should be even higher, as the experimental C=C distance, 1.375 (4) Å, is shorter than the calculated one of 1.396 Å.] The calculated minimum-energy conformation of (c) is planar (see Table 5) and this may be understood if we consider that the steric strains and the hydrogen bond are both optimized in (c) essentially by bond-angle distortions, most notably N(1)-C(1)-C(2), N(2)-C(2)-C(1) and H(N2)-N(2)-C(2). In (b) these bond-angle deformations are minor and the non-bonded interactions are relieved through a twist around the

Table 5. MINDO/3 refined torsion angles (°) for the model compounds (a) [columns (a)1 to (a)3], (b) [columns (b)1 and (b)2] and (c) (see text)

	(a)1	(a)2	(a)3	(b)1	(b)2	(c)
N(1)-C(1)-C(2)-N(2)	-34.43	0.00*	0.00*	-24.42	0.00*	-5.47
N(1)-C(1)-C(2)-N(3)	142.44	180.00*	180.00*	159.86	180.00*	177.58
O(1)-N(1)-C(1)-C(2)	-6.29	-39.91	-2.91*	-5.32	-5.41	-2.27
O(2)-N(1)-C(1)-C(2)	175.46	145.14	176.55*	175.30	174.73	178.19
Relative ΔH [‡] † (kcal mol ⁻¹)	0.0	3.5	5.0	0.0	1.0	0.0

* Fixed values.

† The ΔH[‡] of the fully refined compound is taken as the reference state for the constrained refinement of the same compound. (a)1 is calculated to be ≈2.3 kcal mol⁻¹ less stable than (b)1.

C=C bond, which requires less deformation energy because of the lower π contribution to the overall bond index.

In summary, polarized push-pull ethylenes present invariably some lengthening of the C=C bond due to the extensive π conjugation, but, as our theoretical calculations confirm, steric compression between *cis* substituents is the major factor responsible for the observed twist of the ethylenic moiety. Planar conformations are permitted only if intramolecular hydrogen bonds are present and steric interferences are low.

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* Here and in the following we refer to the calculated difference in the standard enthalpies of formation.

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Structure of Dibenzo[*def,i*]naphtho[1,8,7-*vw*x]pyranthrene

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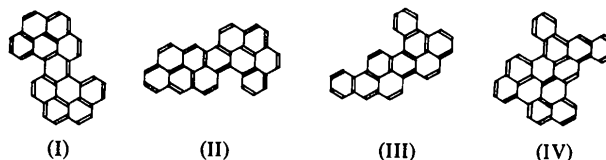
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(Received 28 January 1986; accepted 29 April 1986)

Abstract. $C_{42}H_{20}$, $M_r = 524.6$, orthorhombic, $Pn2_1a$, $a = 22.52$ (1), $b = 21.313$ (7), $c = 4.950$ (4) Å, $V = 2375.9$ (8) Å³, $Z = 4$, $D_m = 1.46$, $D_x = 1.467$ g cm⁻³, $\lambda(\text{Cu K}\alpha) = 1.5418$ Å, $\mu = 6.52$ cm⁻¹, $F(000) = 1088$, $T = 298$ K. Final $R = 0.044$ for 1442 independent reflections. The molecule is largely distorted from a planar structure owing to the steric repulsion between the intramolecular overcrowded atoms. The deviations of the atoms from the mean molecular plane range from 1.07 (1) to -0.74 (1) Å. Molecules are stacked face-to-face to make a columnar structure along the c axis. The distance between the mean molecular planes is 3.60 Å.

Introduction. In a serial study of the molecular distortion due to 1,7-interaction, the crystal structures of three compounds have already been determined: (I) diphenanthro[5,4,3-*abcd*:5',4',3'-*ijklm*]perylene (DPP) (Oonishi, Fujisawa, Aoki & Danno, 1978); (II) anthra[2,1,9,8-*hijkl*]benzo[*de*]naphtho[2,1,8,7-*stuv*]pentacene (1,11-BisoVEB) (Fujisawa, Oonishi, Aoki, Ohashi & Sasada, 1982); and (III) dibenzo[*a,rst*]naphtho[8,1,2-*cde*]pentaphene (VEB) (Oonishi, Fujisawa, Aoki, Ohashi & Sasada, 1986). Recently the title compound, (IV), has been prepared from the condensation of 13*H*-dibenz[*a,de*]anthracen-13-one and 7*H*-benzo[*hi*]chrysen-7-one with zinc dust in the

presence of ZnCl₂ and NaCl. In order to compare its structure with those of the compounds mentioned above, a crystal structure analysis has been carried out.



Experimental. Reddish-brown needle-like crystals from *o*-dichlorobenzene solution; D_m by flotation in ZnCl₂ solution; systematic absences: $0kl$, $k+l = 2n+1$, $hk0$, $h = 2n+1$; crystal dimensions 0.6 × 0.2 × 0.1 mm; Rigaku AFC-6 diffractometer; graphite monochromator; cell parameters refined by least-squares method on the basis of 25 independent 2θ values; $41 < 2\theta < 57^\circ$, intensity measurement performed up to $2\theta = 125^\circ$; range of hkl 0 to 25, 0 to 24 and 0 to 5; $\omega-2\theta$ scan, scan speed $4^\circ \text{ min}^{-1}(\theta)$, scan width $(1.50 + 0.45 \tan \theta)^\circ$; background 5 s before and after each scan; three standard reflections monitored every 100 reflections, no significant variation in intensities; 1878 reflections measured, 1442 with $|F_o| > 3\sigma(|F_o|)$ considered observed and used for structure determination; corrections for Lorentz and polarization,