

of the unsaturated rings. The figure shows the ability of ethylenediamines to mimic the shape of the rigid molecule. In particular the distances d_{N-CG} , between the N atom and the centres of gravity (CG) of the unsaturated rings in cyproheptadine are 6.29 and 6.24 Å, while the corresponding values are N-CG(thenyl) = 6.8 and N-CG(pyridyl) = 5.56 Å in histadyl and N(3)-CG(Ph1) = 6.18 and N(3)-CG(Ph2) = 5.90 Å in antazoline. Thus an N-CG distance of 6.0–6.5 Å is reproduced by the (ring)-CH₂-N-CH₂-CH₂-N⁺ or (ring)-N-CH₂-CH-N⁺ arrangements and probably by both if small conformational changes are allowed. This result seems to be of some interest as it has been shown that d_{N-CG} values of 6.00–6.40 Å can be reproduced by other antihistamines having four-membered propylamino (ring)-CH-CH₂-CH₂-N⁺ or propenylamino (ring)-C=CH-CH₂-N⁺ chains (James & Williams, 1974a, b) and also by the five-membered aminoethyl chain (ring)-CH-O-CH₂-CH₂-N⁺ present in carbinoxamine (Bertolasi *et al.*, 1980b), the correct d_{N-CG} distance being obtained through a zig-zag planar conformation in the former and a helical one in the latter.

In conclusion, all the data so far collected seem to substantiate the idea that a distance of 6.00–6.40 Å between the amino N and the centre of gravity of an unsaturated ring is the primary stereochemical requirement a molecule must fulfill for showing strong antihistaminic activity, all other factors known to affect the biological response (pK_a values, overall lipophilicity

or presence of a second unsaturated ring) being considered mere modulators of the activity itself.

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Structures of Radical Anion Salts and Complexes. 5,5-Dimethyldibenzophospholium 7,7,8,8-Tetracyano-*p*-quinodimethanide (1:2)

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Abstract. C₁₄H₁₄P⁺.2C₁₂H₄N₄^{1/2-}, (DMDBP) (TCNQ)₂, $M_r = 621.6$, monoclinic, space group $P2_1/m$, $a = 7.547$ (4), $b = 30.19$ (2), $c = 7.863$ (5) Å, $\beta = 115.86$ (7)°, $U = 1612.1$ Å³, $Z = 2$, $D_m = 1.30$, $D_c = 1.28$ Mg m⁻³, $F(000) = 642$, $\mu(\text{Mo } K\alpha)$, $\lambda = 0.71069$ Å) = 0.09 mm⁻¹. The structure was solved by direct methods and refined to $R = 0.095$ for 1081 observed reflexions. The radical anions stack plane-to-plane in columns parallel to **c**, each column

consisting of a series of TCNQ dimers. The columns are arranged in sheets parallel to the *ac* plane, with successive sheets being interleaved along **b** by the DMDBP cations.

Introduction. The crystal structure of (DMDBP) (TCNQ)₂ has been determined as part of a series of studies on conducting TCNQ salts (Ashwell, 1978, 1981, 1982). A common feature of these materials is a

characteristic plane-to-plane stacking of the radical anions in columns which gives rise to anisotropic properties. The structural criteria for metallic behaviour are (i) a uniform spacing and (ii) an exocyclic bond to quinonoid ring overlap of adjacent molecules along the conducting chains. Non-uniformity of spacing results in semiconducting behaviour. (DMDBP) (TCNQ)₂ is a small-band-gap semiconductor. The electrical conductivity along *c*, the direction of stacking, varies as $\sigma = \sigma_0 \exp(-E_a/kT)$ where $\sigma_{300K} = 0.3 \text{ S m}^{-1}$ and $E_a = 0.20 \text{ eV}$ ($1 \text{ eV} = 1.60 \times 10^{-19} \text{ J}$).

Black crystals of (DMDBP) (TCNQ)₂ were obtained when a hot acetonitrile solution (200 cm³) of 5,5-dimethyldibenzophospholium iodide (0.2 g) and 7,7,8,8-tetracyano-*p*-quinodimethane (0.2 g) was allowed to cool slowly to ambient temperature. The space group and unit-cell parameters were obtained from oscillation and Weissenberg photographs. Intensities were collected in the range $1^\circ > \theta > 28.5^\circ$ from a crystal *ca* 0.36 × 0.07 × 0.48 mm, mounted with its *a* axis coincident with the ω axis of a Stoe STADI-2 two-circle diffractometer using Mo *K* α radiation and the background- ω -scan-background technique. The crystal diffracted weakly and of the 3061 unique reflexions measured only 1081 had significant counts [$I \geq 2\sigma(I)$]. The intensities were corrected for Lorentz and polarization factors but not for absorption.

The systematic absences, $0k0$, $k = 2n + 1$, do not distinguish between the space groups $P2_1$ and $P2_1/m$. A trial structure was initially attempted in the non-centrosymmetric space group $P2_1$. Multisolution direct

Table 1. Final fractional positional parameters and equivalent isotropic temperature factors ($\times 10^4$) with *e.s.d.*'s in parentheses

The U_{eq} values were calculated by reference to Willis & Pryor (1975).

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}(\text{\AA}^2)$
C(1)	3715 (20)	5917 (4)	9465 (15)	401 (57)
C(2)	2247 (20)	5615 (4)	8335 (16)	371 (56)
C(3)	2734 (20)	5257 (4)	7556 (16)	395 (61)
C(4)	4763 (19)	5167 (3)	7935 (15)	276 (47)
C(5)	6217 (19)	5470 (4)	9076 (16)	328 (51)
C(6)	5744 (19)	5831 (4)	9808 (16)	390 (56)
C(7)	3231 (21)	6298 (4)	10169 (16)	419 (58)
C(8)	1221 (30)	6396 (5)	9648 (22)	585 (79)
C(9)	4641 (24)	6616 (4)	11258 (20)	461 (70)
C(10)	5251 (21)	4792 (4)	7156 (18)	393 (62)
C(11)	3811 (24)	4484 (4)	5990 (18)	411 (62)
C(12)	7234 (21)	4717 (4)	7406 (16)	368 (60)
N(1)	-348 (24)	6516 (5)	9314 (19)	725 (78)
N(2)	5782 (23)	6874 (4)	12146 (19)	649 (73)
N(3)	2635 (20)	4242 (4)	5007 (18)	599 (61)
N(4)	8820 (24)	4637 (4)	7661 (19)	635 (70)
C(13)	5582 (19)	2055 (3)	3974 (14)	304 (44)
C(14)	7429 (19)	2251 (3)	4950 (16)	347 (47)
C(15)	9087 (22)	1979 (4)	5821 (19)	476 (66)
C(16)	8708 (21)	1529 (4)	5685 (16)	489 (66)
C(17)	6855 (22)	1341 (4)	4737 (19)	492 (61)
C(18)	5224 (23)	1619 (4)	3906 (17)	505 (62)
C(19)	1930 (29)	2500	3852 (23)	608 (98)
C(20)	2606 (29)	2500	509 (19)	418 (80)
P	3806 (6)	2500	3027 (5)	252 (8)

Table 2. Details of molecular planes

Asterisks denote atoms not defining the plane.

(a) TCNQ

$$\text{Equation of plane} \\ 0.2465X + 0.5248Y + 0.8147Z - 3.8281 = 0$$

Distances from the plane (Å)

C(1)	-0.02 (1)	C(9)	0.08 (1)*
C(2)	-0.02 (1)	C(10)	0.01 (1)
C(3)	0.02 (1)	C(11)	0.03 (1)*
C(4)	0.00 (1)	C(12)	0.10 (1)*
C(5)	-0.01 (1)	N(1)	0.27 (1)*
C(6)	-0.01 (1)	N(2)	0.11 (1)*
C(7)	0.03 (1)	N(3)	0.07 (1)*
C(8)	0.16 (2)*	N(4)	0.10 (1)*

(b) Cation

Equations of planes

$$(i) 0.5461X + 0.0000Y - 0.8377Z + 0.7990 = 0$$

$$(ii) 0.5336X - 0.0325Y - 0.8451Z + 1.0819 = 0$$

Distances from the planes (Å)

Plane (i)†		Plane (ii)	
C(13)	0.00	C(13)	0.03 (1)
C(14)	0.00	C(14)	-0.01 (1)
C(15)	0.00 (2)*	C(15)	0.00 (2)
C(16)	-0.05 (1)*	C(16)	0.00 (1)
C(17)	-0.07 (2)*	C(17)	0.01 (2)
C(18)	-0.10 (1)*	C(18)	-0.02 (1)
P	0.007 (4)*	P	0.006 (4)*

†Including symmetrically related atoms C(13') and C(14').

methods using *SHELX* (Sheldrick, 1976) enabled the positions of all non-H atoms to be readily located. The two independent TCNQ molecules in the asymmetric unit were so closely related by a mirror plane passing through the cation that analysis was continued in the centrosymmetric space group $P2_1/m$. Coordinates for the H atoms were calculated (C-H = 1.08 Å). Common isotropic temperature factors were applied to the methyl and ring H atoms and refined to final values of $U = 0.062$ (19) and 0.066 (17) Å² respectively. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974) and the weighting scheme was $w = 5.3159/[\sigma^2(F_o) + 0.0010(F_o)^2]$. Full-matrix least-squares refinement with anisotropic temperature factors for the non-H atoms gave the final $R = 0.095$. The final difference map showed no peaks greater than 0.44 e \AA^{-3} .

Significant errors in the atomic coordinates, bond lengths and angles led to a further attempt at refinement in $P2_1$. However, the final R value showed no improvement ($= 0.095$) and in the light of high correlation between the refined parameters, unrealistic temperature factors and unsatisfactory TCNQ geometries we believe $P2_1/m$ to be the more appropriate space group. The final atomic coordinates are listed in Table 1 and the results of least-squares-planes' calculations are in Table 2.*

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36863 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. The crystal structure of (DMDBP)(TCNQ)₂, projected along **a*** and **b**, is shown in Figs. 1 and 2 respectively. The TCNQ molecules are stacked plane-to-plane in columns parallel to **c**, each column consisting of a series of TCNQ dimers. While the overlap between molecules within the dimeric unit is of the ring-external-bond type there is little direct overlap between adjacent dimers (Fig. 3). The mean perpendicular intra-dimer spacing is 3.17 Å. Adjacent TCNQ columns form sheets parallel to the *ac* plane, successive sheets being separated along **b** by the DMDBP cations.

The dimensions of the cation (Fig. 4) closely resemble those found in 5-(*p*-bromobenzyl)-5-phenyldibenzophospholium bromide (Allen, Nowell, Oades & Walker, 1978). The P atom lies 0.007 Å out of the C(13), C(14), C(14'), C(13') plane. The six-membered rings are inclined at an angle of 2.0 (2)° to this plane and 3.7 (5)° to each other. The C-P-C exocyclic bond angles are in the range 107.6 to 114.2°, while the endocyclic angle is 95.6 (4)° and may be compared with values of 93.4° in 5-hydroxy-5*H*-dibenzophosphole 5-oxide (de Boer & Bright, 1974)

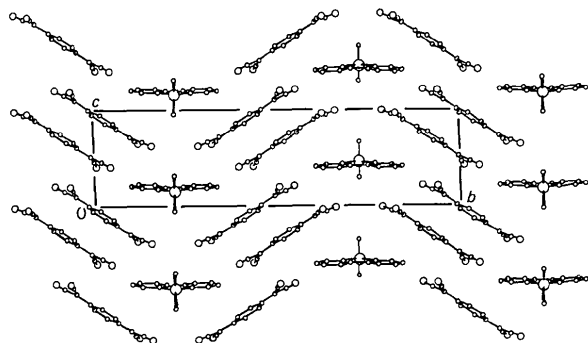


Fig. 1. Projection of the structure along **a***.

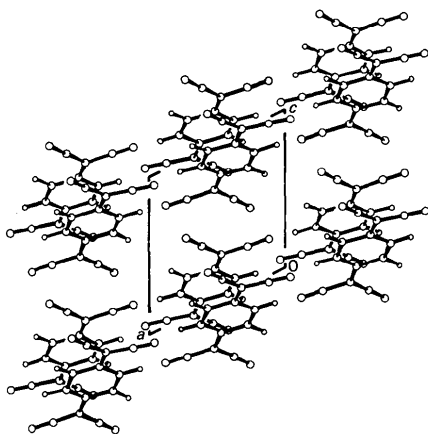


Fig. 2. Projection of the structure along **b**, showing the arrangement of dimers within the TCNQ sheet. For clarity the cation has been omitted.

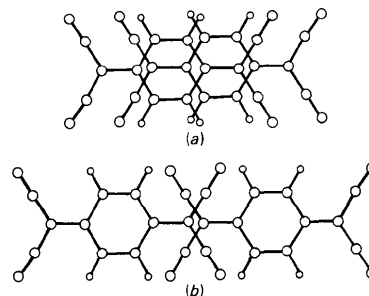


Fig. 3. Molecular overlaps within the TCNQ sheets; (a) the intra-dimer overlap and (b) the inter-dimer overlap.

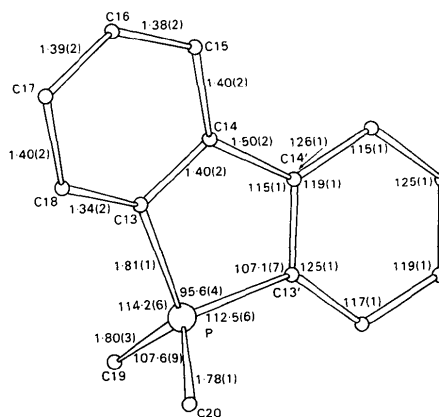


Fig. 4. Bond lengths (Å) and angles (°) in DMDBP with e.s.d.'s in parentheses.

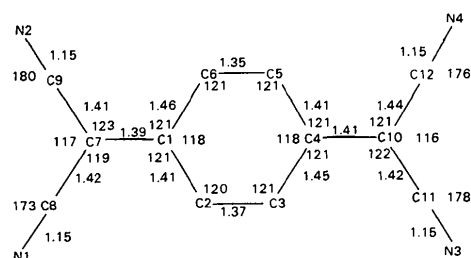


Fig. 5. Bond lengths (Å) and angles (°) in TCNQ. E.s.d.'s are 0.02 Å and 1° respectively.

and 93.9° in 5-(*p*-bromobenzyl)-5-phenyldibenzophospholium bromide. The small endocyclic angle implies strain within the dibenzophospholium system.

The radical anion (Fig. 5) shows no abnormal dimensions and is in agreement with the geometry of TCNQ^{1/2-} (Ashwell, Eley, Wallwork & Willis, 1975). However, in view of the large e.s.d.'s an estimation of the negative charge on the radical anion is not possible. In this structure the TCNQ moiety is not planar but adopts a slight boat form.

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Structure of 8,2'-Anhydro-8-mercapto-9- β -D-arabinofuranosylhypoxanthyl(3'-5')-8,2'-anhydro-8-mercapto-9- β -D-arabinofuranosyladenine (I^{spA}) Hexahydrate*†

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Abstract. C₂₀H₂₀N₉O₉PS₂·6H₂O, triclinic, *P*1, *M*_r = 733·6, *a* = 14·324 (5), *b* = 11·130 (3), *c* = 5·794 (1) Å, α = 97·40 (3), β = 87·42 (3), γ = 120·05 (4)°, *Z* = 1, *D*_m = 1·630 (1), *D*_x = 1·536 Mg m⁻³. The final *R* value is 0·066 for 2697 observed reflections. The molecular conformation is a folded form, with (*g*⁺, *t*) torsion angles around P–O bonds, which is stabilized by hydrophobic interactions between sugar and base moieties and by intermolecular base stacking.

Introduction. It has been reported that the nucleic acid with high-*anti* orientation possesses an interesting tendency to form a left-handed duplex by CD measurement (Uesugi, Yasumoto, Ikehara, Fang & Ts'o, 1972) and energy calculations (Fujii & Tomita, 1976). In the previous paper, we reported the molecular structure of A^{spA} [8,2'-*S*-cyclo-2'-thioadenovyl(3'-5')-8,2'-*S*-cyclo-2'-thioadenosine] which did not have the left-handed stacking form but had a new type of stable non-helical 'bent' form (Fujii, Hamada, Miura, Uesugi, Ikehara & Tomita, 1982).

* (6a*S*, 7*R*, 8*R*, 9a*R*)-4-Amino-6a,7,8,9a-tetrahydro-7-hydroxyfuro[2'.3':4,5]thiazolo[3,2-*e*]purin-3-ium-8-ylmethyl (6a*S*, 7*R*, 8*R*, 9a*R*)-3,4,6a,7,8,9a-hexahydro-8-hydroxymethyl-4-oxofuro[2',3':4,5]thiazolo[3,2-*e*]purin-7-yl phosphate hexahydrate. (The abbreviation I in I^{spA} stands for inosine - 9- β -D-ribofuranosylhypoxanthine.)

† Structure of a Dinucleoside Monophosphate Having a High-*anti* Configuration. II.

I^{spA} was synthesized by condensation of 8,2'-*S*-cycloinosine and 8,2'-*S*-cycloadenosine 5'-monophosphate (Ikehara, Uesugi & Shida, 1980). By slow evaporation of an aqueous solution of I^{spA} in the refrigerator, prismatic transparent crystals were obtained. The intensity data (using a crystal 0·74 × 0·52 × 0·33 mm, sealed in a quartz capillary with some mother liquor) were collected on a Rigaku Denki automatic four-circle diffractometer with Cu *K* α radiation. The ω scanning technique was employed at a rate of 8° min⁻¹.

The structure was solved by the direct method employing the program *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). An *E* map derived from the set with the highest combined figure of merit showed many peaks corresponding to one P atom, two S atoms and some light atoms. Successive Fourier syntheses revealed the remaining non-hydrogen atoms, including six water molecules. After refinements with anisotropic temperature parameters, a difference Fourier synthesis showed all H-atom positions, except those of the water molecules. Final refinement, by a block-diagonal least-squares method with anisotropic thermal parameters for non-hydrogen atoms and with isotropic thermal parameters for H atoms, reduced *R* and *R*_w to 0·066 and 0·089, respectively. The atomic scattering factors in *International Tables for X-ray Crystallography* (1974) were used. All the computations were performed on an ACOS-700 computer of the Crystallographic Research