of the phenyl rings is determined by the close contacts they make with atoms in adjacent molecules.

We thank Professor R. A. Shaw for suggesting the problem and for valuable comments, Dr S. S. Krishnamurthy for the crystals and Professors C. C. Patel and A. R. Vasudeva Murthy for their interest.

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The Crystal and Molecular Structures of Three Cyclopolymethylenetetrazole Compounds

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(*Received* 11 *September* 1978; *accepted* 30 *January* 1979)

Abstract

Trimethylenetetrazole (I), $C_4H_6N_4$, crystallizes in the monoclinic system, space group $P2_1/n$, with a = 7·758 (5), b = 10·367 (6), c = 6·694 (2) Å, β = 102·02 (4)°, 292 K, D_x = 1·389 Mg m^{-3}, Z = 4. Pentamethylenetetrazole (II), $C_6H_{10}N_4$, crystallizes in the monoclinic system, space group $P2_1/n$, with a = 13·310 (6), b = 8·409 (3), c = 6·589 (2) Å, β = 94·72 (3)°, 297 K, D_x = 1·249 Mg m^{-3}, Z = 4. 8-*tert*-Butylpentamethylenetetrazole (III), $C_{10}H_{18}N_4$, crystallizes in the monoclinic system, space group $P2_1/c$, with a = 12·881 (4), b = 6·614 (2), c = 14·132 (6) Å, β = 111·52 (2)°, 291 K, D_x = 1·152 Mg m^{-3}, Z = 4. The X-ray intensities were measured with a Picker FACS-I automatic diffractometer, Mo $K\alpha$ radiation, and θ–2θ scans: (I) 1213 unique data for $2\theta \leq 55°$ (638 observed); (II) 1693 unique data for $2\theta \leq 55°$ (887 observed); (III) 1980 unique data for $2\theta \leq 50°$ (1245 observed). The parameters were refined by full-matrix least squares to a final R of (I) 0·053, (II) 0·055, (III) 0·043. The atoms N(1) and C(5) of the tetrazole ring are disordered in all three structures; they were refined as composite 'NC' atoms consisting of $\frac{1}{2}$N + $\frac{1}{2}$C in their scattering factors. The unusual aqueous solubility of (II) is discussed in relation to the crystal structure. Differences are noted in the molecular structures of complexed and free ligand (II).

0567-7408/79/061413-07$01.00

Introduction

Cyclopolymethylenetetrazoles are noted for their strong stimulating activity on the central nervous system. In sufficient doses they are capable of inducing epileptic convulsions. The activity increases with the length of the hydrocarbon chain and varies from 1000 mg kg^{-1} for trimethylenetetrazole to 30 mg kg^{-1} for heptamethylenetetrazole (Stone, 1970).

As expected, the aqueous solubility decreases with increasing length of the hydrocarbon chain; trimethylenetetrazole (I) is soluble to the extent of 1·4 molal while the solubility of heptamethylenetetrazole is 0·18 molal. A glaring exception is pentamethylenetetrazole (II) which is soluble to the extent of 5·0 molal (Baum, 1976).

Crystallographic studies of the pentamethylenetetrazole (II) complex with iodine chloride (Baenziger, Nelson, Tulinsky, Bloor & Popov, 1967) showed that (II) acts as a monodentate ligand and coordinates through N(4) of the tetrazole ring. In the silver complex, $AgNO_3.2(II)$ (Bodner & Popov, 1972), monodentate tetrazoles are coordinated to the silver atom *via* N(4) and bridging tetrazoles are linked to silver atoms *via* N(3) and N(4). It was of interest to determine the crystal structure of the free ligand to see if there were any changes in the configuration of the molecule upon complexation.

Previous studies have indicated that tri- (Baum, 1976) and pentamethylenetetrazole (Smetana, 1977) form dimers in aqueous solution which may be related to the high solubility of these two compounds. When a *tert*-butyl group is substituted for a hydrogen in the 8 position (III), the solubility in water decreases tremendously to ~3 × 10^{-3} molal. Solvation of these compounds is expected to be due primarily to dipole–dipole interactions, but the dipole moments of these tetrazole compounds are all near 6 D (20 × 10^{-30} Cm) (Popov & Holm, 1962) and one would expect similar solvation effects. Therefore, it was of interest to us to examine the crystal structures of these compounds for features which can help to explain the unusual solubility characteristics of these compounds.

Table 1. *Crystal data, intensity data collection parameters*

	(I)	(II)	(III)
Formula	$C_4H_6N_4$	$C_6H_{10}N_4$	$C_{10}H_{18}N_4$
M_r	110·12	138·17	194·28
$F(000)$	232	296	424
a (Å)	7·758 (5)	13·310 (6)	12·881 (4)
b (Å)	10·367 (6)	8·409 (3)	6·614 (2)
c (Å)	6·694 (2)	6·589 (2)	14·132 (6)
β (°)	102·02 (4)	94·72 (3)	111·52 (2)
V (Å^3)	526·6	735·0	1120·0
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$
Z	4	4	4
D_x (Mg m^{-3})	1·389	1·249	1·152
Background count time (s) (each)	10	10	20
Scan range to which the α_1–α_2 divergence was added (°2θ)	1·00	1·20	1·30
2θ limit (°)	55·00	55·00	50·00
Number of unique data	1213	1693	1980
Number of [$I > 2\sigma(I)$] data	638	887	1245

Experimental

Trimethylenetetrazole (I) (Aldrich) was recrystallized from a 5:1 mixture of carbon tetrachloride and ethanol, m.p. 383 K, lit. 383 K (Kereszty & Wolf, 1935); pentamethylenetetrazole (II) (Aldrich) was recrystallized from diethyl ether and dried under vacuum, m.p. 333 K, lit. 332 K (Knoll Chemische Fabriken, 1928); and 8-*tert*-butylpentamethylenetetrazole (III) was prepared (Baum, 1976) according to the method of D'Itri (D'Itri, 1968; D'Itri & Popov, 1968), m.p. 406 K, lit. 405·5–406·0 K (Harvill, Roberts & Herbst, 1950).

Crystals of these three compounds were grown from covered dilute solutions of the tetrazoles (~0·05 molal) in ether (I and II) or in acetone (III) from which the solvent was permitted to evaporate slowly to dryness. Single crystals were mounted for each compound. Mounting method, approximate dimensions, μ for Mo $K\alpha$: (I) capillary under vacuum (to minimize the apparent air decomposition), 0·2 × 0·2 × 0·2 mm, 0·061 mm^{-1}; (II) glass fiber, 0·1 × 0·2 × 0·4 mm, 0·050 mm^{-1}; (III) glass fiber, 0·2 × 0·3 × 0·5 mm, 0·041 mm^{-1}. The space groups were determined by the monoclinic symmetry and the diffraction conditions: (I, II) $0k0$: $k = 2n$, $h0l$: $h + l = 2n$, $P2_1/n$; (III) $0k0$: $k = 2n$, $h0l$: $l = 2n$, $P2_1/c$. Diffraction data were measured with a Picker FACS-I automatic diffractometer using zirconium-filtered (II) or graphite-monochromatized (I, III) Mo $K\alpha$ radiation. The cell parameters were determined by a least-squares fit to the angular settings of 12 reflections in the range 35° ≤ 2θ ≤ 40° for which the α_1–α_2 doublet was clearly resolved (λ for Mo $K\alpha_1$ = 0·70926 Å). The unique reflections in the $+h +k \pm l$ region were collected by θ–2θ scans [1·0°(2θ) min^{-1}] with three standard reflections measured after every 50 data to scale the data. The crystal data and the intensity data collection parameters are given in Table 1. The data were reduced and standard deviations calculated as a function of counting statistics as reported previously (Wei & Ward, 1976); the least-squares refinement weights were calculated from the standard deviations of the structure factors by weight = $1/[\sigma^2 + (0{\cdot}02F)^2]$; extinction corrections were not applied to the data; and absorption corrections (Templeton & Templeton, 1973) were applied to (I) and (III), but were inconsequential [maximum and minimum corrections were 1·011 and 1·009 for (I) and 1·010 and 1·004 for (III)] and not applied to (II).

Structure solution and refinement

The crystal structures were solved with *MULTAN* (Germain, Main & Woolfson, 1971). Other programs used in this study included *ORTEP* (Johnson, 1965), the entire system of Allan Zalkin's programs (Zalkin, 1974), and programs written and/or modified locally. A CDC 6500 computer was used.

The structures were refined to convergence by a full-matrix least-squares calculation. As the molecules are symmetrical except for N(1) and C(5) of the tetrazole ring, as the thermal parameters for these two atoms were unusual [B_{iso} of 4·81, 5·59, 4·86 for N(1) and 2·57, 3·47, 3·21 Å^2 for C(5), for (I), (II), (III) respectively], and as the final difference maps showed the largest positive densities to be near C(5) and the largest negative densities near N(1), the refinements were continued after reversing the identities of atoms (1) and (5). The results of these 'reversed' refinements corresponded closely to the earlier refinements indicating that atoms (1) and (5) refine equally well as C and N or as N and C and that, therefore, these two atoms are disordered with approximately 50% occupancy of each atom type at each location. Further refinements, using composite 'NC' atoms ($\frac{1}{2}$N + $\frac{1}{2}$C in their scattering factors) for (1) and (5), gave much better agreement *without* increasing the number of refined parameters. It was noted that C(7) of (I) [along with the associated atoms H(3) and H(4)] has unusual thermal parameters indicating additional possible disorder; this possibility was not investigated. The final-cycle refinement indicators are listed in Table 2, the final atomic parameters of the disorder refinements are listed in Table 3* and the numbering of the atoms is shown in Fig. 1. The scattering factors of Doyle & Turner (1968) were used for the non-hydrogen atoms, those of Stewart, Davidson & Simpson (1965) for hydrogen, the anomalous-scattering factors of Cromer & Liberman (1970) for the non-hydrogen atoms, and anomalous-scattering factors of zero were assumed for hydrogen.

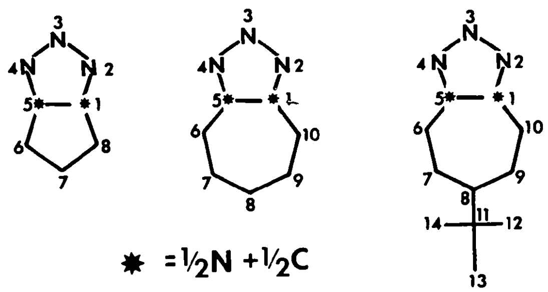

Fig. 1. The numbering of the atoms: (*a*) (I); (*b*) (II); (*c*) (III).

Discussion

The cyclopolymethylenetetrazole molecules (I, II, III) each contain a planar tetrazole ring as shown in Fig. 2; the polymethylene ring in (I) is planar to within ±0·02 Å and lies 0·5° from the plane of the tetrazole ring; the polymethylene rings in (II) and (III) are planar only to within ±0·36 Å (seven-membered rings in chair form) and lie approximately 24° from the planes of the tetrazole rings. The least-squares-planes information is listed in Table 4; bond distances and angles are given in Table 5.

The bond distances in the tetrazole rings range from 1·307 to 1·340 Å with e.s.d.'s of 0·002 to 0·003 Å. The relative average lengths of these bonds are in agreement with the disordered model in which all bonds, except NC(1)—NC(5), are averages of single and double bonds. The bond angles in the tetrazole rings range from 104·5 to 111·6° with e.s.d.'s of 0·2 to 0·3°.

* Tables of structure factors, thermal parameters, torsion angles, and distances and angles involving hydrogen atoms, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34242 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Final-cycle refinement indicators*

	(I)[a]	(I)[b]	(I)[c]	(II)[a]	(II)[b]	(II)[c]	(III)[a]	(III)[b]	(III)[c]
$R_1 = (\Sigma \lvert F_o - F_c \rvert)/\Sigma F_o$	0·068	0·070	0·053	0·073	0·067	0·055	0·054	0·055	0·043
$R_2 = \{[\Sigma w(F_o - F_c)^2]/\Sigma w(F_o)^2\}^{1/2}$	0·059	0·066	0·045	0·065	0·060	0·047	0·051	0·053	0·039
R_1 including	0·141	0·136	0·113	0·134	0·124	0·110	0·097	0·095	0·082
n_1 data for	575	575	575	806	806	806	735	735	735
which $I < n_2\,\sigma(I)$	2	2	2	2	2	2	2	2	2
out of n_3 total data	1213	1213	1213	1693	1693	1693	1980	1980	1980
Standard deviation of an observation of unit weight	2·20	2·45	1·69	2·17	2·01	1·57	1·79	1·85	1·37
Shift-to-error ratios:									
maximum (non-H)	0·55	0·90	0·09	0·40	0·16	0·19	0·22	0·36	0·09
average (non-H)	0·09	0·10	0·03	0·07	0·02	0·04	0·04	0·06	0·02
maximum (H)	0·75	1·05	0·45	0·26	0·27	0·35	0·25	0·22	0·12
average (H)	0·20	0·26	0·11	0·10	0·04	0·08	0·05	0·06	0·03
Final difference map:									
maximum positive density (e Å^{-3})	0·42	0·35	0·25	0·42	0·29	0·25	0·35	0·28	0·19
maximum negative density (e Å^{-3})	−0·74	−0·62	−0·26	−0·49	−0·36	−0·28	−0·38	−0·33	−0·19

[a] Atom (1) as 'N', atom (5) as 'C'.
[b] Atom (1) as 'C', atom (5) as 'N'.
[c] Atoms (1) and (5) as composite 'NC' atoms consisting of $\frac{1}{2}$N + $\frac{1}{2}$C in their scattering factors.

Table 3. *Positional parameters*

Calculated standard deviations are indicated in parentheses.

(*a*) (I) $C_4H_6N_4$

	x	*y*	*z*
NC(1)	0·2342 (3)	0·9178 (2)	−0·0015 (4)
N(2)	0·2897 (3)	1·0106 (2)	0·1334 (4)
N(3)	0·2039 (4)	0·9901 (3)	0·2834 (4)
N(4)	0·0987 (3)	0·8885 (3)	0·2459 (3)
NC(5)	0·1205 (3)	0·8451 (2)	0·0651 (3)
C(6)	0·0504 (5)	0·7392 (3)	−0·0752 (5)
C(7)	0·1513 (9)	0·7598 (5)	−0·2438 (9)
C(8)	0·2643 (6)	0·8782 (4)	−0·2028 (5)
H(1)	−0·081 (5)	0·751 (3)	−0·121 (4)
H(2)	0·066 (4)	0·658 (3)	−0·010 (4)
H(3)	0·112 (6)	0·736 (5)	−0·359 (7)
H(4)	0·224 (9)	0·689 (5)	−0·237 (10)
H(5)	0·389 (5)	0·864 (3)	−0·192 (5)
H(6)	0·213 (4)	0·944 (3)	−0·305 (5)

(*b*) (II) $C_6H_{10}N_4$

	x	*y*	*z*
NC(1)	0·3772 (2)	1·0499 (2)	1·2077 (3)
N(2)	0·4049 (2)	0·8969 (3)	1·2038 (4)
N(3)	0·3806 (2)	0·8479 (3)	1·0156 (4)
N(4)	0·3404 (2)	0·9628 (3)	0·9021 (3)
NC(5)	0·3374 (2)	1·0896 (2)	1·0236 (3)
C(6)	0·2948 (3)	1·2445 (3)	0·9587 (5)
C(7)	0·3692 (3)	1·3785 (3)	1·0019 (5)
C(8)	0·3877 (3)	1·4250 (3)	1·2240 (5)
C(9)	0·4430 (3)	1·3042 (4)	1·3593 (5)
C(10)	0·3853 (3)	1·1521 (4)	1·3902 (4)
H(1)	0·273 (2)	1·225 (3)	0·822 (5)
H(2)	0·237 (3)	1·269 (3)	1·038 (5)
H(3)	0·446 (3)	1·329 (4)	0·939 (5)
H(4)	0·347 (2)	1·466 (4)	0·937 (4)
H(5)	0·327 (2)	1·444 (3)	1·278 (4)
H(6)	0·426 (2)	1·519 (4)	1·233 (4)
H(7)	0·458 (3)	1·347 (4)	1·499 (6)
H(8)	0·513 (3)	1·285 (4)	1·303 (6)
H(9)	0·415 (2)	1·093 (3)	1·493 (4)
H(10)	0·315 (3)	1·184 (4)	1·427 (5)

(*c*) (III) $C_{10}H_{18}N_4$

	x	*y*	*z*
NC(1)	0·9065 (1)	1·3410 (3)	0·1067 (1)
N(2)	0·9507 (1)	1·5265 (3)	0·1234 (1)
N(3)	0·9195 (2)	1·6071 (3)	0·1946 (1)
N(4)	0·8575 (2)	1·4779 (3)	0·2224 (1)
NC(5)	0·8500 (2)	1·3108 (3)	0·1669 (1)
C(6)	0·7908 (2)	1·1274 (5)	0·1757 (2)
C(7)	0·7046 (2)	1·0550 (4)	0·0752 (2)
C(8)	0·7521 (2)	0·9576 (3)	0·0019 (1)
C(9)	0·8111 (2)	1·1127 (3)	−0·0411 (2)
C(10)	0·9209 (2)	1·1955 (4)	0·0339 (2)
C(11)	0·6650 (2)	0·8293 (3)	−0·0828 (2)
C(12)	0·7233 (3)	0·7091 (5)	−0·1416 (3)
C(13)	0·6096 (3)	0·6745 (5)	−0·0366 (3)
C(14)	0·5746 (3)	0·9629 (5)	−0·1570 (3)
H(1)	0·756 (2)	1·156 (3)	0·223 (2)
H(2)	0·851 (2)	1·014 (3)	0·208 (2)
H(3)	0·652 (2)	1·170 (3)	0·040 (2)
H(4)	0·660 (2)	0·949 (3)	0·095 (2)
H(5)	0·809 (1)	0·863 (3)	0·041 (1)
H(6)	0·758 (2)	1·228 (3)	−0·074 (1)
H(7)	0·828 (1)	1·053 (3)	−0·095 (1)
H(8)	0·969 (2)	1·084 (3)	0·072 (1)
H(9)	0·961 (1)	1·266 (3)	−0·004 (1)
H(10)	0·783 (2)	0·628 (4)	−0·095 (2)
H(11)	0·748 (2)	0·798 (4)	−0·181 (2)
H(12)	0·669 (2)	0·616 (4)	−0·189 (2)
H(13)	0·564 (2)	0·732 (4)	−0·000 (2)
H(14)	0·667 (2)	0·598 (4)	0·020 (2)
H(15)	0·566 (2)	0·583 (4)	−0·090 (2)
H(16)	0·609 (2)	1·051 (4)	−0·192 (2)
H(17)	0·537 (2)	1·043 (4)	−0·119 (2)
H(18)	0·520 (2)	0·881 (3)	−0·209 (2)

The average angles indicate that N(3) is displaced towards the NC(1)–NC(5) bond thereby increasing the bond angle at N(3) and decreasing the bond angles at N(2) and N(4) from the overall average value of 108°. The bond angles differ significantly from those in tetrazole (van der Putten, Heijdenrijk & Schenk, 1974) in which the angles at N(2), N(3), N(4) are all approximately 108°. Except for the N(2)–N(3) bond length [reported at 1·30 (1) Å], the tetrazole-ring average bond lengths in (I), (II), (III) agree with those in tetrazole.

The bond lengths in the polymethylene rings appear normal with average NC–NC distances of 1·335 Å, average NC–C distances of 1·471 Å, and average C–C distances of 1·516 Å. The angles in the polymethylene ring of (I) are quite different from those in (II) and (III) and reflect the differences between a planar five-membered ring (I) and the chair-form seven-membered rings (II, III); the only major angular difference between (II) and (III) is C(7)–C(8)–C(9) which in (III) is decreased by the substitution of the *tert*-butyl group at C(8).

The major differences in the molecular structures of the free ligand (II) and the $AgNO_3$ (Bodner & Popov, 1972) and ICl (Baenziger *et al.*, 1967) complexes are due to the disorder of atoms (1) and (5) in the tetrazole ring of (II). The tetrazole-ring bond lengths in (II) relative to those in the two complexes show the averaging of double and single bonds by the disordered structure; the bond angles are essentially the same in the three determinations. The pentamethylene rings are all in the chair form, the average C–C bond lengths are shorter by 0·030 Å in (II), and the bond angles agree rather well except for those at NC(1), NC(5), and C(7) which average 3·1° larger in (II).

The cyclopolymethylenetetrazole molecules (I, II, III) pack together without hydrogen bonding, as shown in Fig. 3. The tetrazole rings of (I) and (II), in adjacent

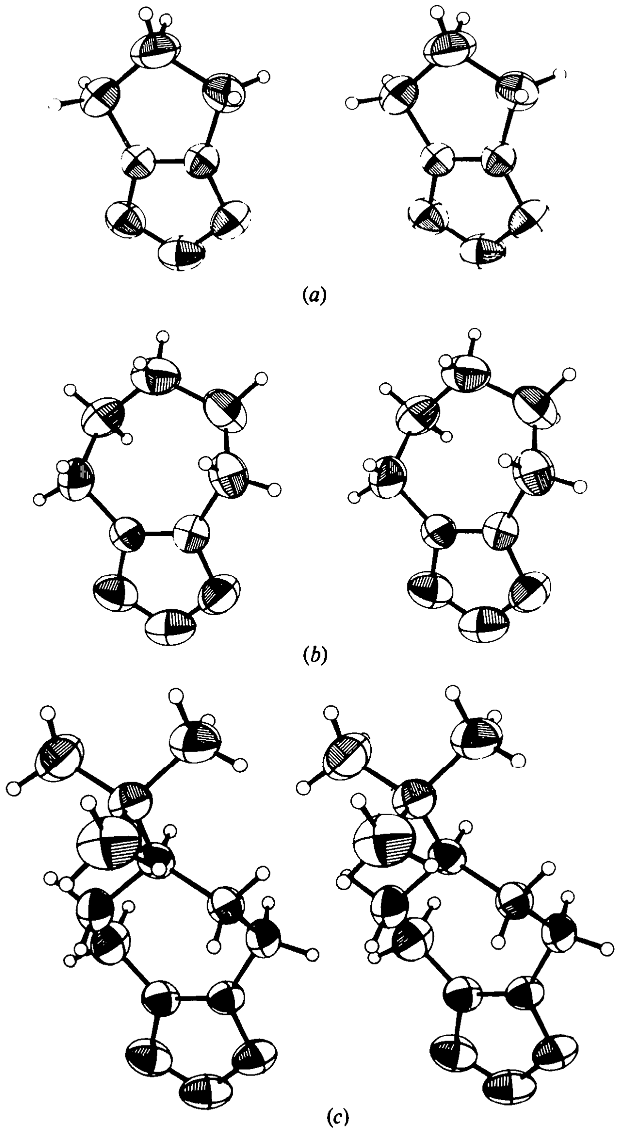

Fig. 2. The molecular structures (*ORTEP*, Johnson, 1965). Ellipsoids drawn at 50% probability level, H atoms assigned $B_{iso} = 0{\cdot}5$ Å^2. (*a*) (I); (*b*) (II); (*c*) (III).

molecules related by a center of symmetry, overlap significantly to produce 'dimers', presumably by dipole–dipole interactions. The distances between the least-squares planes of the tetrazole rings are 3·408 Å for (I) and 3·705 Å for (II) compared with 3·226 Å for tetrazole (van der Putten, Heijdenrijk & Schenk, 1974); the overlaps are illustrated in Fig. 4. 8-*tert*-Butylpentamethylenetetrazole (III) does not crystallize with the tetrazole rings of adjacent molecules parallel to each other; it appears that adjacent molecules, related by twofold screw axes, form 'chains' in which N(3) of one molecule is directed towards the center of the tetrazole ring of the next molecule.

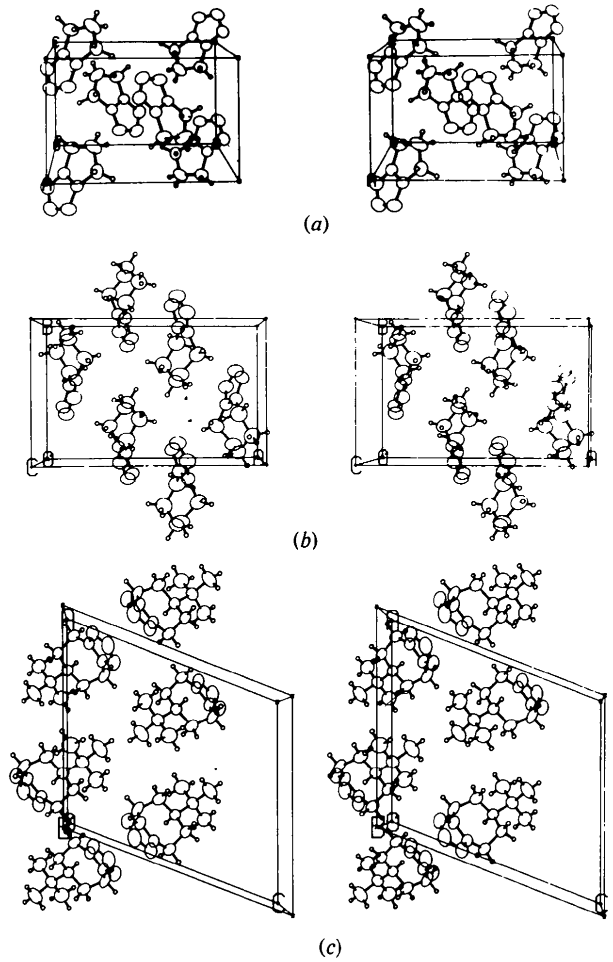

Fig. 3. Packing diagrams (*ORTEP*, Johnson, 1965): (*a*) (I); (*b*) (II); (*c*) (III).

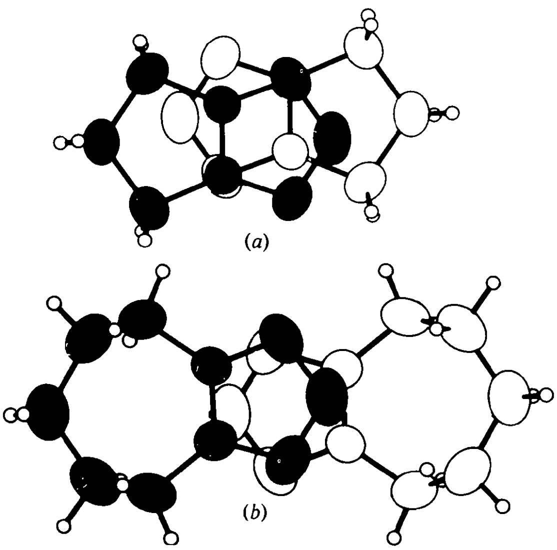

Fig. 4. Overlap of molecules, viewed normal to plane of NC(1), N(3), NC(5) (*ORTEP*, Johnson, 1965): (*a*) (I); (*b*) (II).

Table 4. *Least-squares planes*

Plane 1: tetrazole ring [NC(1), N(2), N(3), N(4), NC(5)].
Plane 2: polymethylene ring [NC(1), NC(5), C(6), C(7), C(8) and C(9), C(10) if present].
Plane 3: tetrazole and polymethylene rings.

Equations of planes with respect to crystallographic axes, x,y,z in fractional coordinates, $Ax + By + Cz - D = 0$

Plane	A	B	C	D
(I)-1	5·144	−6·113	2·095	−4·409
(I)-2	5·169	−6·038	2·120	−4·345
(I)-3	5·161	−6·084	2·095	−4·380
(II)-1	12·364	2·285	−2·154	4·460
(II)-2	12·304	−1·187	−2·827	−0·202
(II)-3	12·626	0·398	−2·569	2·249
(III)-1	7·807	−2·409	6·154	4·503
(III)-2	−6·603	4·656	−3·804	−0·305
(III)-3	−7·301	3·740	−4·939	−1·948

Angles between planes (°)

	(I)	(II)	(III)
1–2	0·5	24·6	−23·8
1–3	0·2	13·4	−13·3
2–3	0·4	11·2	10·5

Distances of atoms from planes (Å)

	(I)-1	(I)-2	(I)-3	(II)-1	(II)-2	(II)-3	(III)-1	(III)-2	(III)-3
NC(1)	−0·000	0·011	0·002	0·001	0·183	−0·172	−0·001	0·158	−0·181
N(2)	0·001	0·023*	0·006	0·002	0·717*	0·127	0·001	0·665*	0·107
N(3)	−0·001	0·022*	0·003	−0·005	1·008*	0·284	0·000	0·977*	0·285
N(4)	0·001	0·012*	−0·000	0·005	0·698*	0·114	−0·001	0·678*	0·117
NC(5)	−0·000	0·004	−0·002	−0·004	0·167	−0·185	0·001	0·161	−0·179
C(6)	−0·008*	−0·017	−0·014	−0·036*	−0·357	−0·495	0·036*	−0·336	−0·477
C(7)	0·032*	0·023	0·028	1·096*	0·277	0·386	−1·082*	0·279	0·379
C(8)	−0·024*	−0·021	−0·023	0·953*	−0·178	0·068	−0·927*	−0·210	0·030
C(9)	–	–	–	1·069*	0·263	0·370	−1·105*	0·286	0·391
C(10)	–	–	–	−0·058*	−0·354	−0·498	0·014*	−0·338	−0·471

* Atom not included in calculation of plane.

Table 5. *Interatomic distances* (Å) *and angles* (°)

	(I) $C_4H_6N_4$	(II) $C_6H_{10}N_4$	(III) $C_{10}H_{18}N_4$
NC(1)–N(2)	1·329 (3)	1·340 (3)	1·337 (2)
NC(1)–NC(5)	1·307 (3)	1·326 (2)	1·322 (2)
NC(1)–C(8)	1·473 (4)	–	–
NC(1)–C(10)	–	1·475 (3)	1·469 (3)
N(2)–N(3)	1·332 (3)	1·322 (3)	1·325 (2)
N(3)–N(4)	1·324 (3)	1·309 (3)	1·324 (3)
N(4)–NC(5)	1·335 (3)	1·336 (3)	1·338 (2)
NC(5)–C(6)	1·473 (3)	1·471 (3)	1·462 (3)
C(6)–C(7)	1·517 (5)	1·511 (4)	1·524 (3)
C(7)–C(8)	1·500 (5)	1·516 (4)	1·527 (3)
C(8)–C(9)	–	1·503 (4)	1·528 (3)
C(8)–C(11)	–	–	1·558 (3)
C(9)–C(10)	–	1·514 (5)	1·525 (3)
C(11)–C(12)	–	–	1·531 (3)
C(11)–C(13)	–	–	1·526 (3)
C(11)–C(14)	–	–	1·530 (3)
N(2)–NC(1)–NC(5)	109·4 (2)	108·3 (2)	108·9 (2)
N(2)–NC(1)–C(8)	137·2 (3)	–	–
N(2)–NC(1)–C(10)	–	125·0 (2)	124·7 (2)
NC(5)–NC(1)–C(8)	113·4 (2)	–	–

	(I) $C_4H_6N_4$	(II) $C_6H_{10}N_4$	(III) $C_{10}H_{18}N_4$
NC(5)–NC(1)–C(10)	–	126·6 (2)	126·3 (2)
NC(1)–N(2)–N(3)	104·8 (3)	105·7 (2)	106·0 (2)
N(2)–N(3)–N(4)	111·6 (3)	111·3 (2)	110·5 (2)
N(3)–N(4)–NC(5)	104·5 (3)	106·1 (2)	106·3 (2)
NC(1)–NC(5)–N(4)	109·7 (2)	108·6 (2)	108·3 (2)
NC(1)–NC(5)–C(6)	113·5 (2)	127·2 (2)	127·4 (2)
N(4)–NC(5)–C(6)	136·9 (3)	124·2 (2)	124·3 (2)
NC(5)–C(6)–C(7)	101·0 (3)	112·0 (2)	113·9 (2)
C(6)–C(7)–C(8)	110·6 (3)	115·2 (3)	115·3 (2)
C(7)–C(8)–NC(1)	101·4 (3)	–	–
C(7)–C(8)–C(9)	–	115·5 (3)	111·6 (2)
C(7)–C(8)–C(11)	–	–	113·3 (2)
C(9)–C(8)–C(11)	–	–	112·5 (2)
C(8)–C(9)–C(10)	–	114·9 (3)	115·8 (2)
C(9)–C(10)–NC(1)	–	112·7 (2)	113·5 (2)
C(8)–C(11)–C(12)	–	–	110·0 (2)
C(8)–C(11)–C(13)	–	–	110·8 (2)
C(8)–C(11)–C(14)	–	–	111·4 (2)
C(12)–C(11)–C(13)	–	–	106·5 (2)
C(12)–C(11)–C(14)	–	–	109·3 (3)
C(13)–C(11)–C(14)	–	–	108·8 (3)

The distances between the centers of the tetrazole rings of the two molecules forming the 'dimers' are 3·481 Å for (I) and 3·741 Å for (II), indicating fairly strong dipole–dipole interactions. The 'dimers' themselves do not interact strongly with each other as indicated by the distances between tetrazole ring centers of 5·401, 5·902 and 6·694 Å for (I) and 5·863, 6·589 and 8·072 Å for (II). Thus, the forces between 'dimers' are weak and this may account for the large solubilities of (I) and (II).

The distances between the centers of the tetrazole rings of the individual molecules of (III) are 4·390 Å along the 'chains' and 6·132, 6·614 and 7·557 Å to other adjacent molecules. It would be expected that the lattice energy of (III) would be higher (interactions at 4·390 Å between individual molecules) than those of (I) or (II) (interactions at 5·4 Å minimum between 'dimers') and, consequently, the solubility of (III) would be less than that of (I) or (II).

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The Crystal Structure and the Twinning of β-9,10-Dichloroanthracene

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(*Received* 30 *August* 1978; *accepted* 12 *March* 1979)

Abstract

β-9,10-Dichloroanthracene, $C_{14}H_8Cl_2$, crystallizes in the triclinic space group $P\bar{1}$. The lattice constants at room temperature are: a = 3·873 (2), b = 8·585 (5), c = 16·727 (7) Å, α = 102·38 (2), β = 95·30 (4), γ = 97·17 (3)°; V = 534·89 Å^3, D_{calc} = 1·534 Mg m^{-3}. The unit cell of β-9,10-dichloroanthracene contains two symmetry-independent molecules, each embodying a crystallographic centre of symmetry. The structure can be described as a stacking of these molecules parallel to the a axis. The distances between adjacent molecules are 3·48 and 3·52 Å respectively. The structure determination by X-ray diffraction resulted in a final residual R = 0·053 for 1476 observed reflections. β-9,10-Dichloroanthracene crystals exhibit a strong tendency for twinning. The twin law can be described by a twofold rotation around the a^* axis. The consistency of the twin law with the structure is discussed.

0567-7408/79/061419-06$01.00