

## The Influence of Substituents on the Equilibrium Bisnorcaradiene $\rightleftharpoons$ [10]Annulene. The Crystal and Molecular Structure of 11-Methyltricyclo[4.4.1.0<sup>1,6</sup>]undeca-2,4,7,9-tetraene-11-carbonitrile

BY RICCARDO BIANCHI, TULLIO PILATI AND MASSIMO SIMONETTA

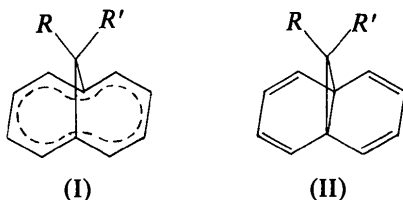
*Istituto di Chimica Fisica dell'Università e Centro CNR, Via Golgi 19, 20133 Milano, Italy*

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$C_{13}H_{11}N$  is triclinic, space group  $P1$ ,  $a = 8.310$  (1),  $b = 7.026$  (2),  $c = 9.508$  (1) Å,  $\alpha = 100.89$  (2),  $\beta = 97.82$  (1),  $\gamma = 113.48$  (1)°,  $Z = 2$ . Refinement of 339 variables with 1939 counter reflexions resulted in  $R_w = 0.040$ . The central bond lengths in the two independent molecules are 1.851 and 1.783 Å. Constrained and conventional least-squares refinements and difference maps confirm the physical meaning of these exceptionally long C–C bonds. The structure is better described as a bisnorcaradiene than as a [10]annulene, at least in the solid phase.

### Introduction

A number of observations (Vogel, 1969) suggested the possibility that the bridged substituted 1,6-methano[10]annulenes exist as [10]annulene (I) or as bisnorcaradiene (II) systems.



The shifting of the equilibrium (I)  $\rightleftharpoons$  (II) towards (II) implies the formation of a cyclopropane ring, so that information on the influence of substituents at C(1) on this equilibrium may be obtained through the study of the influence of the same substituents in cyclopropane. It has been shown (Hoffmann & Davidson, 1971; Hoffmann & Stohrer, 1971) that in cyclopropane the introduction of  $\pi$ -electron-acceptor substituents at C(1) makes the C(2)–C(3) bond stronger, while the introduction of  $\pi$ -electron-donating substituents weakens this bond. This was confirmed in our laboratory by an X-ray diffraction investigation of two derivatives of 1,6-methano[10]annulene: 11,11-difluoro-1,6-methano[10]annulene (hereafter DIF; Pilati & Simonetta, 1976) and 11,11-dimethyltricyclo[4.4.1.0<sup>1,6</sup>]undeca-2,4,7,9-tetraene (DIM; Bianchi, Morosi, Mugnoli & Simonetta, 1973). The first is of type (I), the second of type (II), but with a very long C(1)–C(6) bond. (1.827 and 1.771 Å for the two independent molecules in the asymmetric unit).

Günther & Schmickler (1974) studied the equilibrium (I)  $\rightleftharpoons$  (II) in a number of examples by <sup>13</sup>C NMR

spectroscopy. They showed that the signal of C(1) and C(6) shifts to a lower field when passing from (I) to (II). In particular, for DIM at room temperature the signal falls at 82 p.p.m. and shows a temperature dependence indicating a stabilization of form (I) at low temperature. Analogous phenomena were observed for 11-methyltricyclo[4.4.1.0<sup>1,6</sup>]undeca-2,4,7,9-tetraene-11-carbonitrile (hereafter CNME), the object of the present study. The differences between DIM and CNME are a C(1), C(6) signal at lower field at room temperature (68 p.p.m.) in the latter and an inverse temperature dependence, indicating for CNME a further stabilization of (II) at low temperature. Hence it could be argued that the cyclopropane ring in CNME is more closed than in DIM.

### Experimental

CNME crystallizes in  $P1$ , with  $Z = 2$ . A colourless crystal was enclosed in a thin-walled glass capillary and used for data collection. The lattice parameters obtained by least squares from  $\sin^2 \theta$  values of 48 reflexions in the angular range  $84 < 2\theta < 95^\circ$  (Cu  $K\alpha$ ,  $\lambda = 1.54178$  Å, graphite monochromator) are:  $a = 8.310$  (1),  $b = 7.026$  (2),  $c = 9.508$  (1) Å,  $\alpha = 100.89$  (2),  $\beta = 97.82$  (1),  $\gamma = 113.48$  (1)°,  $D_x = 1.238$ ,  $D_m = 1.233$  g cm<sup>-3</sup> (by flotation in dilute  $K_2HgI_4$ ).

The measurement of intensities was made with a Syntex  $P1$  autodiffractometer operating in the  $\theta/2\theta$  scan mode. The scan range was  $2^\circ$  plus the separation Cu  $K\alpha_1 - Cu K\alpha_2$ ; the scan rate was allowed to vary from 2 to 12° min<sup>-1</sup> as a function of the maximum peak intensity; background was measured on each side of the reflexion for half the total scan time. Two

reference reflexions, measured periodically, did not change significantly. Of 1966 unique measured reflexions ( $2\theta < 140^\circ$ ), 1939 had intensities greater than background; these were classified as observed and used in the refinement. Each reflexion was assigned a variance  $\sigma^2(I)$  based on counting statistics plus a term  $(0.03S)^2$ , where  $S$  is the scan count (Peterson & Levy, 1957). Lorentz and polarization corrections were applied; absorption correction was not considered necessary [ $\mu(\text{Cu } K\alpha) = 5.66 \text{ cm}^{-1}$ ].

### Structure determination and refinement

Analogies between the cell parameters of CNME and DIM suggest isomorphism between the two structures. An  $F_c$  calculation with the scale factor and average isotropic temperature factor obtained from a Wilson plot and the coordinates of the C atoms of DIM gave  $R = 0.29$  for 1939 reflexions. From the subsequent difference map the coordinates of the two N atoms were obtained. Perimetral H atom coordinates were obtained geometrically and those of the methyl-group H atoms from a difference map.

Refinement was carried out initially with geometrical and thermal constraints in different steps. In step *A* the two molecules were considered identical, rigid and of  $m$  symmetry; in step *B* the two molecules were considered to be different; in step *C* the atoms of the substituents at the methano bridges were allowed to shift out of the plane of symmetry and to have independent thermal parameters; finally, in step *D* no constraints were considered: C and N atoms were given anisotropic thermal parameters, H atoms isotropic. In steps *A* and *B* the normal equations were solved by diagonalization of the matrix; in steps *C* and *D* by inversion. In step *D*, because of the high number of parameters, refinement was by block-diagonal least squares, each block

Table 1. *Some refinement characteristics*

$p$  = number of independent parameters refined;  $R = \sum |F_o| - |F_c| / \sum |F_o|$ ;  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o)^2]^{1/2}$ ; goodness of fit =  $[\sum w(|F_o| - |F_c|)^2 / (N - p)]^{1/2}$ . All these quantities were computed only for the reflexions included in the refinement ( $N = 1939$ ).

	$p$	$R$	$R_w$	Goodness of fit
Step <i>A</i>	66	0.070	0.088	3.39
Step <i>B</i>	125	0.053	0.065	2.53
Step <i>C</i>	181	0.046	0.054	2.15
Step <i>D</i>	339	0.035	0.040	1.60

	$A/B$	$A/C$	$A/D$	$B/C$	$B/D$	$C/D$
$\mathcal{R}^*$	1.36	1.63	2.19	1.20	1.62	1.35
$\mathcal{R}(0.001)^*$	1.027	1.047	1.107	1.027	1.087	1.067
$(\mathcal{R} - 1) / [\mathcal{R}(0.001) - 1]^*$	13.1	13.3	11.2	7.5	7.1	5.2

\* See Pawley (1972).

corresponding to an entire molecule. In every step the secondary extinction coefficient was included and refined [ $g = 9(3) \times 10^{-6}$  for set *D*]. Form factors were from Cromer & Waber (1965), except those for H which were from Stewart, Davidson & Simpson (1965). The quantity minimized was  $\sum w(|F_o| - |F_c|)^2$ , with weights  $w = 1/\sigma^2(F_o)$  [where  $\sigma^2(F_o) = \sigma^2(F_o^2)/4F_o^2$ ].

Table 2. *Final coordinates and their e.s.d.'s (set D)*  
( $\times 10^4$  for C and N,  $\times 10^3$  for H)

	$x$	$y$	$z$
Molecule <i>A</i>			
C(1)	7990 (3)	4207 (4)	6465 (2)
C(2)	9687 (3)	5301 (4)	7543 (3)
C(3)	11257 (3)	5432 (5)	7239 (3)
C(4)	11375 (4)	4171 (5)	5932 (3)
C(5)	9930 (4)	2723 (4)	4843 (3)
C(6)	8141 (3)	2585 (4)	4755 (3)
C(7)	6582 (3)	526 (4)	4195 (3)
C(8)	5099 (3)	-28 (4)	4743 (3)
C(9)	4979 (3)	1230 (4)	6056 (3)
C(10)	6346 (3)	3098 (4)	6902 (3)
C(11)	7869 (3)	4614 (3)	4962 (2)
C(12)	9386 (3)	6479 (4)	4816 (3)
C(13)	6145 (3)	4585 (5)	4153 (3)
N	10476 (3)	7965 (4)	4632 (3)
H(2)	964 (4)	593 (5)	854 (3)
H(3)	1241 (3)	635 (4)	800 (3)
H(4)	1250 (4)	419 (5)	593 (3)
H(5)	993 (4)	156 (5)	404 (3)
H(7)	670 (4)	-47 (5)	343 (4)
H(8)	403 (4)	-145 (5)	429 (3)
H(9)	385 (4)	58 (4)	643 (3)
H(10)	633 (4)	370 (4)	787 (3)
H(131)	502 (4)	343 (5)	412 (3)
H(132)	602 (5)	605 (6)	461 (4)
H(133)	614 (4)	465 (5)	313 (4)
Molecule <i>B</i>			
C(1)	-3 (3)	4 (4)	840 (3)
C(2)	-1786 (4)	-1611 (4)	798 (3)
C(3)	-3237 (4)	-2118 (5)	-268 (3)
C(4)	-3157 (4)	-1390 (4)	-1578 (3)
C(5)	-1608 (3)	-150 (4)	-1877 (3)
C(6)	111 (3)	876 (4)	-802 (3)
C(7)	1751 (3)	1141 (4)	-1276 (3)
C(8)	3123 (3)	978 (4)	-476 (3)
C(9)	3044 (3)	278 (4)	844 (3)
C(10)	1578 (3)	-283 (4)	1412 (3)
C(11)	244 (3)	2201 (4)	701 (2)
C(12)	-1267 (3)	2706 (4)	847 (3)
C(13)	1983 (4)	4186 (4)	1502 (3)
N	-2358 (3)	3235 (4)	1019 (3)
H(2)	-196 (4)	-253 (5)	143 (3)
H(3)	-436 (5)	-316 (6)	-18 (4)
H(4)	-430 (4)	-200 (4)	-235 (3)
H(5)	-162 (4)	4 (5)	-292 (4)
H(7)	167 (3)	123 (4)	-239 (3)
H(8)	418 (4)	116 (5)	-87 (3)
H(9)	412 (4)	11 (5)	126 (3)
H(10)	148 (3)	-107 (4)	212 (3)
H(131)	312 (5)	413 (7)	149 (4)
H(132)	206 (6)	478 (7)	252 (5)
H(133)	220 (6)	552 (8)	120 (5)

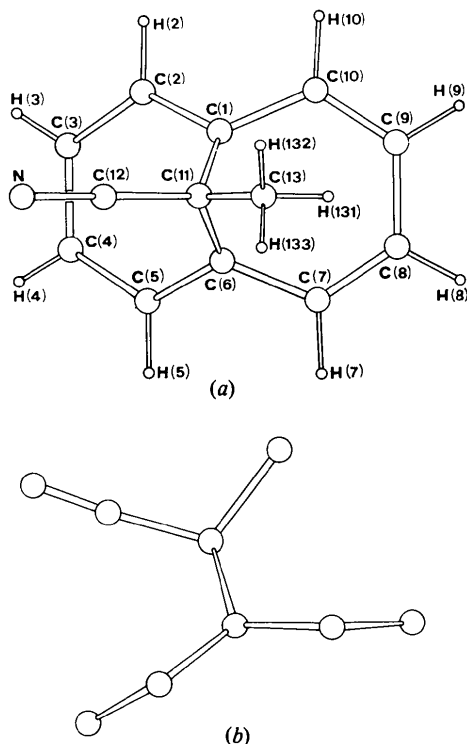


Fig. 1. Molecule *B* seen (a) along the maximum inertial axis with numbering of atoms and (b) along the intermediate inertial axis. In (b) H atoms are omitted.

Table 1 shows some characteristics of the four refinement steps. The last three rows in this table give the *R*-factor ratios  $\mathcal{R}$  among sets *A*, *B*, *C*, and *D*, the theoretical  $\mathcal{R}(0.001)$  (Pawley, 1972) and the ratios  $(\mathcal{R} - 1)/[\mathcal{R}(0.001) - 1]$ . It is evident that the two molecules, on the basis of these tests, are different and that the best set of parameters is obtained in step *D*. The resultant atomic coordinates (step *D*) are presented in Table 2. The final difference map with this set of parameters oscillates in the range  $\pm 0.15 \text{ e } \text{Å}^{-3}$ .

Fig. 1 shows two schematic views of molecule *B* with the numbering of the atoms. The numbering of molecule *A* is identical.\*

### Discussion

The geometrical parameters of the two molecules of CNME are shown in Tables 3, 4 and 5. The geometry of the H atoms is normal and is not reported. In both molecules the methyl groups are in the staggered arrangement with respect to the C atoms bonded at

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33358 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond lengths (Å) and angles (°)

	Molecule <i>A</i>	Molecule <i>B</i>
C(1)–C(2)	1.440	1.453
C(1)–C(10)	1.440	1.456
C(5)–C(6)	1.441	1.452
C(6)–C(7)	1.443	1.446
C(2)–C(3)	1.346	1.341
C(4)–C(5)	1.356	1.340
C(7)–C(8)	1.346	1.339
C(9)–C(10)	1.351	1.345
C(3)–C(4)	1.422	1.433
C(8)–C(9)	1.427	1.432
C(1)–C(11)	1.508	1.508
C(6)–C(11)	1.511	1.514
C(1)–C(6)	1.851	1.783
C(11)–C(12)	1.458	1.451
C(11)–C(13)	1.521	1.519
C(12)–N	1.140	1.128
	Molecule <i>A</i>	Molecule <i>B</i>
C(1)–C(2)–C(3)	123.2	122.4
C(4)–C(5)–C(6)	122.9	122.9
C(6)–C(7)–C(8)	123.7	123.2
C(9)–C(10)–C(1)	123.5	122.9
C(2)–C(3)–C(4)	123.6	124.0
C(3)–C(4)–C(5)	124.2	123.3
C(7)–C(8)–C(9)	123.8	123.8
C(8)–C(9)–C(10)	124.0	123.4
C(2)–C(1)–C(11)	119.7	119.8
C(10)–C(1)–C(11)	118.8	118.9
C(5)–C(6)–C(11)	119.8	118.8
C(7)–C(6)–C(11)	118.9	119.0
C(1)–C(11)–C(12)	115.9	115.9
C(6)–C(11)–C(12)	114.4	116.0
C(1)–C(11)–C(13)	120.0	120.5
C(6)–C(11)–C(13)	120.8	119.9
C(2)–C(1)–C(10)	120.2	119.2
C(5)–C(6)–C(7)	120.3	119.9
C(1)–C(6)–C(11)	52.1	53.7
C(6)–C(1)–C(11)	52.3	54.0
C(1)–C(11)–C(6)	75.6	72.3
C(12)–C(11)–C(13)	107.6	108.7
C(11)–C(12)–N	174.7	175.3

Table 4. Selected torsion angles (°)

	Molecule <i>A</i>	Molecule <i>B</i>
C(1)–C(2)–C(3)–C(4)	12.9	–9.8
C(3)–C(4)–C(5)–C(6)	–12.0	10.6
C(6)–C(7)–C(8)–C(9)	8.5	–7.7
C(8)–C(9)–C(10)–C(1)	–9.7	7.5
C(10)–C(1)–C(2)–C(3)	–146.0	146.2
C(4)–C(5)–C(6)–C(7)	145.6	–145.8
C(5)–C(6)–C(7)–C(8)	–142.2	144.1
C(9)–C(10)–C(1)–C(2)	143.4	–143.1
C(2)–C(3)–C(4)–C(5)	–0.8	–1.1
C(7)–C(8)–C(9)–C(10)	0.9	0.1

C(11). Table 3 gives bond lengths (e.s.d.'s 0.002–0.004 Å) and bond angles (e.s.d.'s 0.1–0.2°). Table 4 gives some selected torsion angles on the perimetral rings. In Table 5 the equations of some least-squares planes through groups of atoms, and dihedral angles are reported.

Table 5. *Some least-squares planes through groups of atoms*

The coefficients  $q_i$  are the direction cosines relative to the crystallographic axes  $a$ ,  $b$  and  $c$  ( $\times 10^4$ ). The distances of the defining atoms from the mean plane involving four atoms are always  $<0.006$  Å.

Plane	Atoms defining plane	Molecule A				Molecule B			
		$q_1$	$q_2$	$q_3$	$d$ (Å)	$q_1$	$q_2$	$q_3$	$d$ (Å)
A	C(1), C(6), C(11)	8303	1360	-315	5.721	9372	-1239	84	0.004
B	C(1), C(2), C(5), C(6)	249	-8575	6057	1.352	-6519	8497	3016	0.239
C	C(1), C(6), C(7), C(10)	6162	-7682	5862	5.424	-60	7700	3013	0.243
D	C(2), C(3), C(4), C(5)	1988	-8767	6352	2.889	-5204	8664	3208	0.034
E	C(7), C(8), C(9), C(10)	5160	-8204	6167	4.980	-1258	8136	3116	0.091

Dihedral angles (°)	Molecule A		Molecule B	
	Molecule A	Molecule B	Molecule A	Molecule B
$A \wedge B$	111.3	110.4	$B \wedge C$	138.5
$A \wedge C$	110.2	110.0	$B \wedge D$	168.8
			$C \wedge E$	170.7
			Molecule A	Molecule B
			171.8	173.1

Table 6. *Comparison of the geometries of CNME, DIM and DIF*

Values are averaged assuming  $mm2$  symmetry. Torsion angles are averaged over their absolute values.

Bond lengths (Å)	CNME	CNME	DIM	DIM	DIF
	Molecule A	Molecule B	Molecule A	Molecule B	
C(1)–C(2)	1.441	1.452	1.453	1.458	1.410
C(1)–C(11)	1.509	1.511	1.507	1.509	1.470
C(1)–C(6)	1.851	1.783	1.827	1.771	2.269
C(2)–C(3)	1.350	1.341	1.348	1.335	1.366
C(3)–C(4)	1.425	1.433	1.431	1.418	1.411
Bond angles (°)					
C(2)–C(1)–C(10)	120.3	119.6	117.8	117.8	126.2
C(2)–C(1)–C(11)	119.3	119.1	120.6	120.4	116.4
C(1)–C(2)–C(3)	123.4	122.9	123.8	123.9	124.2
C(2)–C(3)–C(4)	123.9	123.6	123.6	123.3	127.6
C(1)–C(11)–C(6)	75.6	72.3	74.6	71.8	101.0
Torsion angles (°)					
C(10)–C(1)–C(2)–C(3)	144.3	144.8	139.9	140.2	139.3
C(1)–C(2)–C(3)–C(4)	10.8	8.9	8.3	7.9	15.9

As expected the molecules of CNME in the crystal are of type (II), but with the distances C(1)–C(6) slightly but significantly longer than the equivalent ones in DIM.

Molecule A, with the longer C(1)–C(6) length, has a perimeter slightly but significantly less alternating than B.

The C(1)–C(6) lengths found in CNME are exceptionally long: similar but shorter distances were found in DIM (1.827 and 1.771 Å), bi(anthracene-9,10-dimethylene) photoisomer (1.77 Å, Ehrenberg, 1966) and tricarbonyl(bicyclo[4.4.1]undeca-1,3,5-triene)chromium (1.72 Å, Barrow & Mills, 1971). In CNME the molecular symmetry  $m$  is quite well preserved, while the  $mm2$  symmetry on the tricyclo skeleton is acceptable only to a first approximation because of the different effects of methyl and

ciano groups on the cyclopropane ring. In spite of this we report some geometrical parameters of the tricyclo skeleton of CNME, assuming  $mm2$  symmetry, to permit a more useful comparison with DIM and DIF. Table 6 shows the analogy between CNME and DIM [type (II)] and the marked difference from DIF [type (I)].

The analogy between CNME and DIM is so strong that, comparing the geometrical parameters of the cyclopropane ring in the different molecules, greater difference is found between molecules A and B in the same compound than between the A or B molecules in the two distinct compounds. A qualitative explanation of this unusual feature is that the differences between molecules A and B, both in CNME and in DIM, are due to packing effects: the C(1)–C(6) bond is an oscillator so weak that small differences of environment of the two molecules can strongly affect the equilibrium distance. The weakness of the C(1)–C(6) oscillator can be deduced from experimental data in two distinct ways.

Günther & Schmickler (1974) derived from their <sup>13</sup>C NMR spectra that the energy barrier for the valence tautomerism (I)  $\rightleftharpoons$  (II) in CNME and in DIM is  $<6$  kcal mol<sup>-1</sup>. Because the transformation B  $\rightarrow$  A in CNME and in DIM represents only a small fraction of the transformation (II)  $\rightarrow$  (I), the difference in energy between A and B is expected to be much lower than this. Bianchi *et al.* (1973) calculated the packing energy of the real crystal of DIM and of three different hypothetical crystals in which all molecules were of type A or all of type B, or with A and B exchanged in their barycentre with respect to the real crystal. Assuming zero level for the real crystal, the packing energy of the three hypothetical ones ranges between 0.1 and 0.5 kcal mol<sup>-1</sup>. The differences in electronic energy between A and B are then expected to be of comparable magnitude. This is in line with the existence of different molecules A and B both in DIM and in CNME.

Table 7. Observed and calculated thermal parameters ( $\text{\AA}^2$ ) of the cyclopropane rings ( $\times 10^5$ )

$$T = \exp[-2\pi^2(U_{11}a^{*2}h^2 + \dots + U_{23}b^*c^*kl)].$$

		Molecule A			Molecule B		
		obs.	calc.	obs. - calc.	obs.	calc.	obs. - calc.
				$\sigma(\text{obs.})$			$\sigma(\text{obs.})$
C(1)	$U_{11}$	4584	4490	1.2	5209	5030	2.1
	$U_{22}$	5990	5279	11.1	4796	4970	3.2
	$U_{33}$	4737	4263	4.2	5288	4391	7.7
	$U_{12}$	-183	-46	4.0	-121	-316	7.2
	$U_{13}$	167	188	0.3	219	646	6.5
C(6)	$U_{23}$	703	-156	19.1	-69	-111	1.2
	$U_{11}$	5172	4835	4.0	4578	4652	0.9
	$U_{22}$	4810	5050	4.1	6121	5272	13.7
	$U_{33}$	5680	4462	9.7	4895	4331	5.0
	$U_{12}$	-18	176	6.9	329	43	8.9
C(11)	$U_{13}$	-12	579	8.7	125	296	2.7
	$U_{23}$	414	-9	10.1	-833	184	24.8
	$U_{11}$	4265	4513	3.5	4467	4967	6.8
	$U_{22}$	5056	4993	1.2	4862	4941	1.5
	$U_{33}$	4232	4479	2.5	4478	4660	1.8
	$U_{12}$	-127	70	7.5	25	-272	9.9
	$U_{13}$	187	206	0.3	215	328	1.9
	$U_{23}$	-187	42	6.2	26	-156	4.6

The second way to verify the weakness of the C(1)–C(6) bond comes from the analysis of crystallographic thermal parameters. We attempt to interpret the thermal parameters of CNME in terms of rigid-body motion (Schomaker & Trueblood, 1968). Normally, if the molecule is non-rigid, it can be expected that the differences between observed and calculated  $U_{ij}$ 's increase on going from the internal to the external part of the molecule. However, for both *A* and *B* in CNME the calculated  $U_{ij}$ 's fit well the observed ones for all atoms except C(1), C(6), C(11), C(12) and N, the difference in terms of e.s.d.'s for the first three atoms being the greatest. Table 7 reports observed and calculated  $U_{ij}$ 's and their differences in terms of their e.s.d.'s for these atoms. It can be seen that the cyclopropane ring is not rigid. This is also substantiated from a comparison of the difference maps of the cyclopropane rings obtained from set *C* (**T**, **L**, **S** constrained) and set *D*. While the map obtained from set *D* does not present any particular feature, the map from set *C* (Fig. 2) does: peaks and troughs indicate clearly that the anisotropic thermal factors derived with **T**, **L**, **S** constrained are underestimated for C(1) and C(6) along a direction in the planes of Fig. 2 approximately perpendicular to C(1)–C(11) and C(6)–C(11), respectively, confirming that the equilibrium distance C(1)–C(6) is an average over values much more spread with respect to the normal situation. Peaks and troughs in this difference map cannot be interpreted as residues of bent bonds. One could think that the structure can be interpreted as a mixture of rigid molecules of type (I) and type (II) with a shorter C(1)–C(6) distance, of which our model is a superposition. No attempt in this direction was made, since

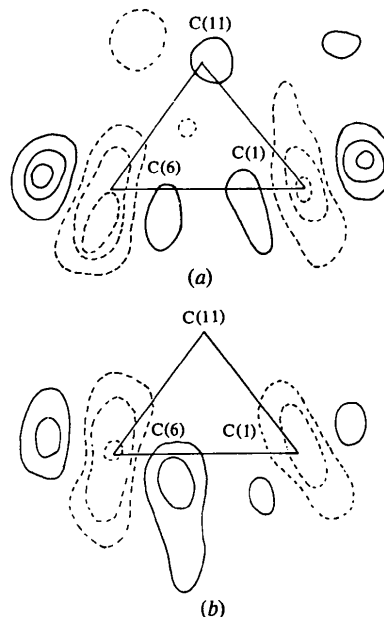


Fig. 2. Difference map obtained from parameters of step *C*. The plane corresponds to the cyclopropane ring of (a) molecule *A*, and (b) molecule *B*. Contour levels are at intervals of  $0.05 \text{ e \AA}^{-3}$  (solid lines positive, dashed lines negative, zero contours omitted).

the irregularities in the  $U_{ij}$ 's of C(1) and C(6) and the residuals on the difference map (Fig. 2) are too small to justify this approach. Therefore, our conclusion is that in crystals of CNME only molecules of type (II) exist while C(1)–C(6) is an oscillator so weak that its experimental equilibrium lengths have a spread wider than in normal C–C bonds.

## References

- BARROW, M. J. & MILLS, O. S. (1971). *J. Chem. Soc. A*, pp. 1982–1986.
- BIANCHI, R., MOROSI, G., MUGNOLI, A. & SIMONETTA, M. (1973). *Acta Cryst.* **B29**, 1196–1208.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- EHRENBERG, M. (1966). *Acta Cryst.* **20**, 182–186.
- GÜNTHER, H. & SCHMICKLER, H. (1974). Paper presented at the 2nd International Symposium on Non-benzenoid Aromatic Compounds (ISNA II), Lindau, 23–27 September.
- HOFFMANN, R. & DAVIDSON, R. B. (1971). *J. Am. Chem. Soc.* **93**, 5699–5705.
- HOFFMANN, R. & STOHRER, W. D. (1971). *J. Am. Chem. Soc.* **93**, 6941–6948.
- PAWLEY, G. S. (1972). *Advances in Structure Research by Diffraction Methods*. Vol. 4, pp. 1–64, New York: Pergamon Press.
- PETERSON, S. W. & LEVY, H. A. (1957). *Acta Cryst.* **10**, 70–76.
- PILATI, T. & SIMONETTA, M. (1976). *Acta Cryst.* **B32**, 1912–1913.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
- VOGEL, E. (1969). *Pure Appl. Chem.* **20**, 237–262.

*Acta Cryst.* (1978). **B34**, 2162–2165

**Experimental and Theoretical Difference Densities for Cyanuric Acid.  
A Simple Refinement of Density Distributions of Bonding Electrons VI. Comparison of  
Observed and Calculated Electron Densities VIII**

BY C. SCHERINGER, A. KUTOGLU AND E. HELLNER

*Fachbereich Geowissenschaften, Universität Marburg, D-3550 Marburg, Federal Republic of Germany*

AND H. L. HASE, K.-W. SCHULTE AND A. SCHWEIG

*Fachbereich Physikalische Chemie, Universität Marburg, D-3550 Marburg, Federal Republic of Germany*

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From a recently refined model of the electron density distribution in cyanuric acid, dynamic and static density sections are calculated and are presented as difference densities  $\rho(\text{molecule}) - \rho(\text{isolated atoms})$ . The sections obtained are compared with the results of other workers, and with corresponding sections derived from a new quantum-chemical calculation of 4-31G quality. In addition, a direct examination of this theoretical density distribution with the X-ray data is described.

### Introduction

Since Verschoor & Keulen (1971) collected X-ray data of cyanuric acid at 100 K, this molecule has been the subject of several electron density studies. Coppens & Vos (1971) determined the positional and thermal parameters at 125 K by neutron analysis, and McIver, Coppens & Nowak (1971) presented an INDO calculation of the density distribution in the molecule. The dynamic difference density of the molecule obtained from a minimum basis set STO-3G calculation (R. F. Stewart, unpublished) was given by Jones, Pautler & Coppens (1972). Moreover, these authors determined the population parameters of

orbital products from Verschoor & Keulen's (1971) X-ray data, *i.e.* they refined a quantum-chemical model from the experimental data. Kutoglu & Hellner (1978) determined the density distribution in the molecule by means of an empirical model from Verschoor & Keulen's (1971) X-ray data. In this paper the dynamic and static difference densities obtained from Kutoglu & Hellner's (1978) refinement are given. Theoretical static and dynamic (Hase, Reitz & Schweig, 1976) difference densities obtained from a new quantum-chemical calculation with a 4-31G basis set are presented and compared with the corresponding experimental densities. An additional test of the theoretical density distribution against Verschoor & Keulen's (1971) X-