

## The Crystal and Molecular Structure of *trans*-3,4-Di-*t*-butylcyclobutanedione

BY J. K. COLEMAN, S. C. NEELY AND DICK VAN DER HELM\*

Chemistry Department, University of Oklahoma, Norman, Oklahoma 73069, U.S.A.

(Received 12 February 1975; accepted 23 May 1975)

The crystal and molecular structure determination is reported for *trans*-3,4-di-*t*-butylcyclobutanedione (C<sub>12</sub>H<sub>20</sub>O<sub>2</sub>). The crystals are monoclinic, space group *C2/c* with  $a = 10.063$  (1),  $b = 7.7273$  (5),  $c = 16.190$  (2) Å,  $\beta = 98.811$  (7)°,  $Z = 4$ . Intensity data were collected for all reflections with  $2\theta$  less than 150° using Ni-filtered Cu  $K\alpha$  radiation. The final  $R$  value is 0.060 for the 1274 data. The cyclobutane ring is non-planar with a dihedral angle of 174.3°. The longest and shortest bonds in the cyclobutane ring are 1.560 (3) and 1.527 (2) Å. The estimated standard deviations are between 0.002 and 0.003 Å for all non-hydrogen bond distances.

### Introduction

The structure of 3,4-di-*t*-butylcyclobutanedione (DTCD) was determined to support the MO and spectral studies of the compound (Coleman, 1975). Conjugation of a diketone system with other double bonds in a molecule may cause a red shift of the  $n-\pi^*$  absorption band. Saturated compounds, however, normally show this transition band at 480 m $\mu$  or less (Nagakara & Kuboyana, 1954). DTCD has an  $n-\pi^*$  absorption maximum at an unusually long wavelength (536 m $\mu$ ) compared with other saturated unsubstituted  $\alpha$ -diketones (Birnbaum, Cookson & Levin, 1961). It appears as though the *t*-butyl groups play an important role in causing the high  $\lambda_{\max}$  for DTCD since the corresponding absorption maximum of 487 m $\mu$  for 1,2-cyclobutanedione occurs near the normal absorption range (Heine, 1971). It has been shown that  $\sigma$  bonds play an important role in interactions between  $\pi$ -MO's in  $\alpha$ -diketones (Neely, Fink, van der Helm & Bloomfield, 1971). It is known that such interactions also depend on the dihedral angle between the carbonyl groups (Leonard & Mader, 1950). The bond length and bond angle data for DTCD were necessary in order to study both the conformational and  $\sigma$  bond effects on the  $n-\pi^*$  transition energies.

### Experimental

The compound was obtained from Professor H. Wynberg who reported the synthesis and spectra (de Groot, Oudman & Wynberg, 1969). A suitable data crystal was obtained by equilibrium diffusion of water into an ethanol-water solution of the compound. The crystal was enclosed in a thin-walled capillary because it proved too volatile at normal room temperature and pressure.

All X-ray data of the block-like (0.4 × 0.4 × 0.3 mm)

\* Supported by N.I.H. Development Award K4-GM-42,572.

pink crystal were measured on a Nonius CAD-4 automatic diffractometer using Ni-filtered Cu  $K\alpha$  radiation ( $\lambda = 1.5418$  Å), at room temperature (26°C). The density measurement and cell volume data (Table 1) indicated that the unit cell contained four molecules. The molecule therefore contains a twofold axis coincident with one of those of the space group. The least-squares cell dimensions were obtained from the averages of the  $\pm 2\theta$  values of 40 reflections. The 1274 intensity data taken comprised all unique reflections with  $2\theta$  less than 150°. The data were collected with  $\theta-2\theta$  scans in which the  $\theta$  scan width (°) was calculated as  $1.0 + 0.1 \tan \theta$ . The maximum scan time was 150 s with  $\frac{2}{3}$  of the time spent scanning the peak, while  $\frac{1}{3}$  each was used on the left and the right backgrounds. 296 reflections were considered indistinguishable from the background, having  $I < 2.0 \sigma(I)$ . For the purpose of least-squares refinement, these reflections were assigned a value equal to 1.4 times the square root of the total count ( $T$ ). Secondary extinction corrections were made on the observed intensities according to the equation  $I_{\text{corrected}} = I \exp(-C_{\text{ext}}P)$ . The constant  $C_{\text{ext}}$  was determined to be  $5 \times 10^{-7}$  from the slope of a plot of  $\log F_o/F_c$  versus  $P$  (net count) for reflections having  $F_o$  greater than 30. Absorption corrections were omitted.

Table 1. *Crystal data*

Formula: C<sub>12</sub>H<sub>20</sub>O<sub>2</sub>

F.W. 196.29

Systematic absences:  $hkl$ :  $h+k=2n+1$   
 $h0l$ :  $l=2n+1$  ( $h=2n+1$ )  
 $0k0$ :  $k=2n+1$

Space group: *C2/c*

$a = 10.063$  (1) Å

$b = 7.7273$  (5)

$c = 16.190$  (2)

$\beta = 98.811$  (7)°

$D_m = 1.048$  g cm<sup>-3</sup> (by flotation in aqueous sodium sulfate solution)

$D_x = 1.048$  g cm<sup>-3</sup>

$Z = 4$

$V = 1244.1$  Å<sup>3</sup>

## Structure determination

The O–O and C–C (ring) vectors were identified on the  $v=0$  section of the Patterson synthesis. By building a model it was possible to postulate C and O atom positions and to compare interatomic vectors for these on the Patterson map. This model was used in an initial structure factor calculation. The temperature parameters of the non-hydrogen atoms were made isotropic and the  $R$  index [ $R = \sum(|kF_o| - |F_c|) / \sum|kF_o|$ ] which had an initial value of 0.55, dropped to 0.16 after a few cycles of least-squares refinement. At this point the temperature parameters of the non-hydrogen atoms were made anisotropic and the  $R$  subsequently decreased to 0.12. All hydrogen atoms were located from a difference Fourier synthesis, and were included in the least-squares refinement. The extinction correction yielded the final  $R$  value of 0.060 for all data while the  $R$  for the reflections with  $I > 2\sigma(I)$  is 0.046. The final difference Fourier showed no negative or positive peaks greater than  $0.15 \text{ e } \text{Å}^{-3}$ . The parameter shifts in the final least-squares cycle were all less than  $0.25\sigma$ .

All least-squares refinements were made using the block-diagonal least-squares program of Ahmed (1966), while using  $9 \times 9$  and  $4 \times 4$  blocks. A logical routine (van der Helm & Nicholas, 1970), which may exclude certain reflections from least-squares refinement, was used during the refinement. The final positional and thermal parameters and their estimated standard deviations are given in Tables 2 and 3.\* The atomic scattering factors for C and O were taken from *International Tables for X-ray Crystallography* (1962). The scattering factors for hydrogen atoms were those of Stewart, Davidson & Simpson (1965).

A weighting scheme was used which assigns an experimental weight to each structure factor as defined below:

$$W_F = 1/\sigma_F^2$$

$$\sigma_F = \frac{1}{2} \left[ \frac{\sigma^2 + (0.04P)^2}{(P)(L_p)} \right]^{1/2}$$

\* The final  $F_o$  and  $F_c$  tables have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31164 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Parameters for the carbon and oxygen atoms

$x$ ,  $y$  and  $z$  are expressed in fractions of the cell edges. The anisotropic temperature factors are expressed in the form:  $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*) \times 10^{-4}]$ . Standard deviations for the last digit are given in parentheses.

	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
O(1)	-0.1278 (2)	-0.1238 (2)	0.2988 (1)	1217 (12)	758 (8)	1643 (17)	-357 (8)	478 (12)	104 (9)
C(2)	-0.0602 (2)	-0.0134 (2)	0.2751 (1)	683 (8)	547 (8)	861 (10)	-100 (7)	123 (8)	49 (8)
C(3)	-0.0565 (1)	0.1841 (2)	0.2781 (1)	463 (6)	524 (7)	589 (8)	0 (5)	133 (5)	25 (6)
C(4)	-0.0276 (2)	0.2620 (2)	0.3664 (2)	686 (9)	766 (10)	594 (8)	-86 (8)	216 (7)	-65 (8)
C(5)	0.0955 (2)	0.1783 (4)	0.4172 (1)	807 (12)	1644 (22)	638 (10)	-54 (13)	21 (9)	-25 (12)
C(6)	-0.1500 (2)	0.2296 (3)	0.4099 (1)	901 (13)	1220 (17)	782 (12)	-30 (11)	409 (10)	-3 (11)
C(7)	-0.0082 (3)	0.4567 (3)	0.3585 (2)	1662 (23)	828 (14)	1053 (16)	-366 (14)	665 (17)	-398 (12)

Table 3. Parameters of the hydrogen atoms

The  $x$ ,  $y$  and  $z$  are expressed in fractions of the cell edges. Standard deviations for the last digit are given in parentheses.

	$x$	$y$	$z$	$B$
H(8)	-0.139 (2)	0.236 (2)	0.250 (1)	5.3 (3)
H(9)	0.177 (2)	0.194 (3)	0.391 (1)	8.3 (5)
H(10)	0.113 (3)	0.218 (3)	0.473 (2)	10.8 (7)
H(11)	0.088 (3)	0.049 (3)	0.420 (2)	10.4 (6)
H(12)	-0.134 (2)	0.281 (3)	0.470 (2)	9.7 (6)
H(13)	-0.157 (2)	0.099 (3)	0.417 (1)	8.2 (5)
H(14)	-0.234 (2)	0.281 (3)	0.378 (2)	10.3 (7)
H(15)	0.003 (2)	0.509 (4)	0.408 (2)	11.5 (7)
H(16)	0.066 (2)	0.480 (3)	0.328 (1)	9.1 (5)
H(17)	-0.088 (4)	0.527 (6)	0.325 (3)	18.8 (12)

in which  $\sigma = T^{1/2}V$ ,  $V$  = scan speed,  $T$  = total count,  $P = [P_k - 2(R + L)]$ ,  $R$  = right background count,  $L$  = left background count,  $L_p$  = Lorentz and polarization corrections,  $P_k$  = peak count.

In the structure factor analysis the average values of  $W_F(\Delta F)^2$  did not show a significant variation with either  $|F_o|$  or  $\sin \theta/\lambda$ , validating the weighting scheme used.

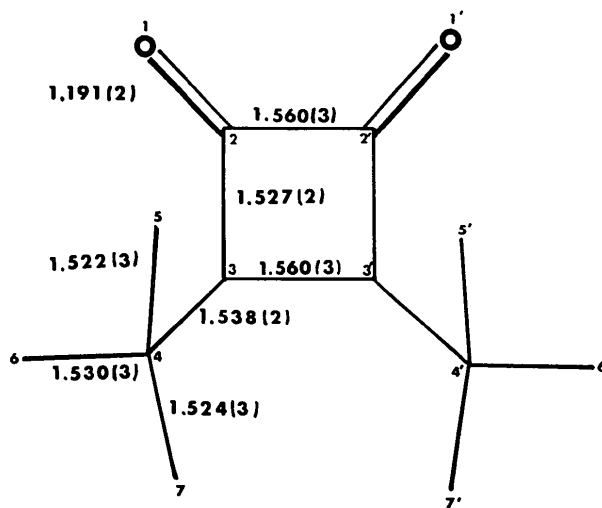


Fig. 1. Bond distances, not involving hydrogen. The standard deviations of the last digits are given in parentheses.

## Description of the structure

The bond distances are shown in Fig. 1 and Table 4. The bond angles are listed in Table 5.

Table 4. C-H bond lengths (Å)

The standard deviations for the last digit are given in parentheses.			
C(3)-H(8)	0.97 (2)	C(6)-H(13)	1.02 (2)
C(5)-H(9)	0.99 (2)	C(6)-H(14)	1.00 (3)
C(5)-H(10)	0.94 (3)	C(7)-H(15)	0.88 (3)
C(5)-H(11)	1.00 (3)	C(7)-H(16)	0.97 (2)
C(6)-H(12)	1.04 (3)	C(7)-H(17)	1.05 (5)

Table 5. Bond angles (°)

The standard deviations for the last digit are given in parentheses.			
O(1)C(2)C(3)	136.0 (2)	C(2)C(3)H(8)	112.7 (9)
O(1)C(2)C(2')	134.1 (2)	C(3)C(4)C(5)	111.0 (2)
C(3)C(2)C(2')	89.9 (1)	C(3)C(4)C(6)	108.2 (1)
C(2)C(3)C(3')	89.9 (1)	C(3)C(4)C(7)	108.4 (2)
C(2)C(3)C(4)	114.8 (1)	C(5)C(4)C(6)	109.1 (2)
C(4)C(3)C(3')	119.4 (1)	C(5)C(4)C(7)	111.1 (2)
C(4)C(3)H(8)	107.0 (10)	C(6)C(4)C(7)	108.9 (2)
C(3')C(3)H(8)	112.4 (10)		

Cyclobutane rings exist in both planar and puckered conformations. Infrared and Raman studies have indicated that the non-planar conformation of these rings is more favorable than the planar conformation (Rathjens, Freeman, Gwinn & Pitzer, 1953), but most of the reported centrosymmetrically substituted rings are planar in the solid state (Shirrell & Williams, 1974a). Therefore, it was not surprising to find that *trans*-3,4-di-*t*-butylcyclobutanedione (DTCD, Fig. 2) has a non-planar ring conformation (Table 6). The ring carbons are 0.028 Å (over nine standard deviations) out of the least-squares plane, calculated for C(2), C(3), C(2') and C(3'). The dihedral angle between the plane through C(3), C(2) and C(2') and the plane through C(3), C(3') and C(2') is 174.3° (2). The reported dihedral angles for puckered cyclobutane rings range from 145° to 161° (Shirrell & Williams, 1973). The dihedral angle of DTCD is large for puckered ring conformations, and this is probably due to the diketone substitution. The dihedral angle between the carbonyl groups, *i.e.* the torsion angle O(1)-C(2)-C(2')-O(1'), is 7.6°.

Table 6. Least-squares planes

Plane	Equation	Constant
I	C(2) C(3) C(2') C(3')	5.494x + 0.000y + 12.052z = 3.013
II	C(3) C(2) C(2')	5.185x - 0.283y + 12.424z = 3.110
III	C(2') C(3') C(3)	-5.789x - 0.283y - 11.649z = -2.964
IV	O(1) C(2) C(3) C(2')	5.123x - 0.338y + 12.492z = 3.124

*x*, *y* and *z* are fractional coordinates.

Distances from planes (Å)

	I	IV
O(1)	-0.114	-0.004
C(2)	-0.028	0.009
C(3)	0.028	-0.002
O(1')	0.114	0.085
C(2')	0.028	-0.002
C(3')	-0.028	-0.125
C(4)	1.252	
C(5)	2.540	
C(6)	1.103	
C(7)	1.263	

Two long C-C bond lengths of 1.560 (3) Å are found for C(2)-C(2') and C(3)-C(3'). Long bond lengths in cyclobutane rings are common (Dunitz & Schomaker, 1952), usually in the range from 1.547 to 1.58 Å (Shirrell & Williams, 1973). A short bond length of 1.527 (2) Å is observed for C(2)-C(3) which is symmetrically identical with the bond C(2')-C(3'). The shortening of this bond is consistent with the significant overlap of the *p*- $\pi$  atomic orbital on C(2) with  $\sigma$ -hybrid orbitals on C(3) as reported for a similar diketone by Neely *et al.* (1971). Shirrell & Williams (1974a, b) have reported a short bond occurring in the ring of two other cyclobutanedione structures: the corresponding bond lengths are 1.515 (6) Å for 2,2,4,4-tetramethyl-3-thio-1,3-cyclobutanedione, and 1.507 (2) Å for 2,2,4,4-tetramethyl-1,3-cyclobutanedione.

The shortest bond not involving hydrogen in the compound is, as expected, the carbonyl bond length, C(2)-O(1). The length of 1.191 (2) Å is shorter than the average carbonyl bond length of 1.215 Å reported by Sutton (1965). This apparent shortening may well be caused, in part or completely, by the high thermal

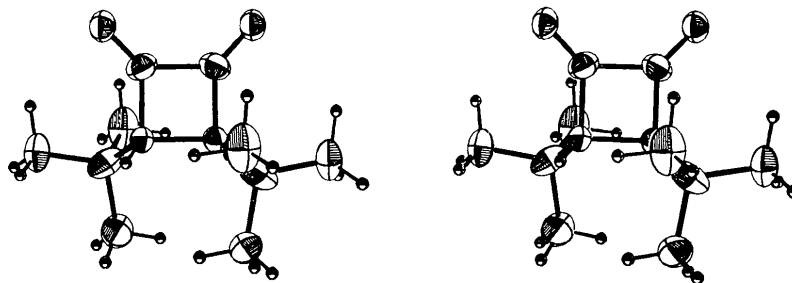


Fig. 2. An ORTEP stereographic drawing of DTCD.

motion of the oxygen atom (Table 2), although other short carbonyl bond lengths have been reported for similar systems (Fink, van der Helm & Neely, 1975; Shirrell & Williams, 1974b). Other atoms in the molecule show high thermal motion as well (Table 2). Two ring carbons, C(3) and C(3'), show the least thermal motion, while two *t*-butyl atoms, C(5) and C(7) show the highest. An apparent shortening of the C–C bonds occurs throughout the *t*-butyl groups. This is probably caused by the large thermal motion of the *t*-butyl carbons, especially for C(5) and C(7), which are involved in the shortest C–C bonds. It is interesting to note that the *t*-butyl carbon, C(6), closest to the oxygen, O(1), shows the least vibration of the three methyl groups. Also, the hydrogen H(13) bonded to C(6) (Fig. 3) presents the shortest intramolecular distance between the oxygen atom and a methyl hydrogen atom. This distance of 2.63 (2) Å is comparable to the van der Waals distance of 2.6 Å (Pauling, 1960).

A rigid-body calculation was carried out using the method of Schomaker & Trueblood (1968) with the appropriate restrictions imposed for a molecule with *C*<sub>2</sub> point symmetry. The r.m.s.  $\Delta U_{ij}$  was 0.0043 Å<sup>2</sup>, whereas the r.m.s.  $\sigma U_{ij}$  was 0.0011 Å<sup>2</sup>. This indicates that the molecule does not behave as a rigid body and the associated bond distance corrections can therefore not be made.

The shortest non-bonding intramolecular distance in DTCD occurs between two hydrogens. The nearly perfect staggering of the C–C and C–H bonds in the *t*-butyl group causes H(9') on C(5') to be only 2.29 (2) Å from H(8) on C(3) (Fig. 3). This is somewhat shorter than the van der Waals distance of 2.4 Å between two hydrogen atoms, and suggests some intramolecular overlap.

The shortest intermolecular distance observed is the distance between the ring hydrogen, H(8), of one molecule and an oxygen atom (O'') of a symmetry-related molecule ( $-\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$ ) (Fig. 4). While this distance of 2.59 (2) Å indicates relatively little interaction, the fact that the ring hydrogen is the most acidic (Reid, 1968) and that the C(3)–H(8) and H(8)–O'' vectors are collinear cannot be ignored [C(3)–H(8) = 0.97, C(3)–O'' = 3.55 Å]. A point of interest is that the only other intermolecular distances less than 3.00 Å are also H–O'' distances. These distances are 2.75 and 2.99 Å and involve H(9) and H(17) respectively. All intermo-

lecular distances not involving hydrogens are greater than 3.5 Å.

The bond angles in the *t*-butyl group for the non-hydrogen atoms range from 108.2° to 111.1° (Table 5) and average 109.45°. The bond angles involving the methyl hydrogen atoms have an average value of 109.4°. All four of the angles in the cyclobutane ring are equal with a value of 89.9 (1)°.

Atoms O(1), C(2), C(3) and C(2') are relatively coplanar. The three angles, O(1)–C(2)–C(3), O(1)–C(2)–C(2'), C(3)–C(2)–C(2'), in this plane differ, as expected, from the normal 120°. The respective values of 136.0 (2)°, 134.1 (2)° and 89.9 (1)° reflect the expected strain in a four-membered ring. Similar angles for other ring diketones have been reported. Fink *et al.* (1975), reported the corresponding angles of 134.2 (2)°, 135.5 (2)° and 90.3 (1)° for an  $\alpha$ -diketone; Shirrell & Williams (1974b), reported 131.9 (2)°, 134.6 (2)° and 93.5 (1)° for a 1,3-diketone.

The C–H bond distances average 0.99 Å, the extremes being 0.88 (3) Å for C(7)–H(15) and 1.05 (5) Å for C(7)–H(17). The carbon involved in both cases, C(7), has the highest thermal motion for the molecule.

## Discussion

The structure of DTCD provides information for at least two interesting questions arising in the earlier investigations of de Groot *et al.* (1969). The first point occurs in the report of the compound's preparation

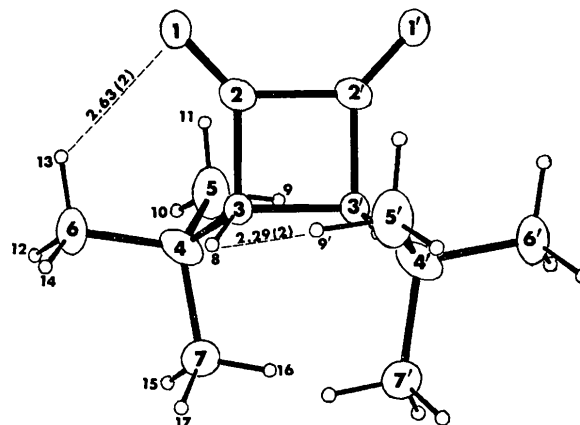


Fig. 3. Intramolecular distances involving the hydrogen atoms.

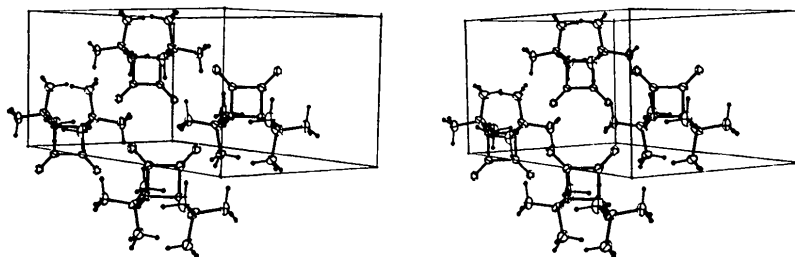


Fig. 4. An ORTEP drawing of the packing of the molecules.

from a mixture of ( $\pm$ ) and *meso* diesters. The reacting form was postulated to be ( $\pm$ ) and the structure determination indeed verifies that assumption. The second, and perhaps more interesting question arises in the comparison of the electronic spectrum of DTCD with those obtained for the tricyclo[4,4,2,0<sup>1,6</sup>]dodeca-3,8-diene-11,12-dione (2DB), and its tetrahydro derivative (ODB). It is interesting to note that the DTCD spectrum corresponds closely to that of the unsaturated  $\alpha$ -diketone (2DB) rather than to the saturated compound (ODB), as might be expected. Both the 536  $m\mu$  for DTCD and the 537.5  $m\mu$  for 2DB (Bloomfield, 1968a; Bloomfield & Moser, 1968b) are above the expected maximum of 480  $m\mu$  for an  $n-\pi^*$  transition for unsubstituted  $\alpha$ -diketones (Nagakara & Kuboyana, 1954, *cf. Introduction*).

Although a detailed comparison of the forementioned compounds is beyond the scope of this paper, some of the structural similarities of DTCD and 2DB are noted: both compounds have short carbonyl bond lengths of 1.19 Å; both have C-C bond shortening occurring in the ring; both have nonplanar carbonyl dihedral angles, although the carbonyls of 2DB are in a planar ring, while the carbonyls of DTCD are in a nonplanar ring; both compounds show intramolecular interaction between an oxygen atom and a hydrogen bonded to a carbon atom. It would not be surprising to find that many of these structural similarities contribute to the spectral similarities of DTCD and 2DB. Indeed, MO studies (Coleman, 1975) show that the *t*-butyl groups influence the electronic state in such a way as to give a similar influence on the  $n-\pi^*$  transition as that reported for the unsaturated 2DB compound (Neely *et al.*, 1971).

We give special thanks to Professor H. Wynberg for providing a sample of the title compound. We also thank the University of Oklahoma for making computer time available to us.

#### References

- AHMED, F. R. (1966). *SFLS* Program, NRC-10, National Research Council, Ottawa.
- BIRNBAUM, H., COOKSON, R. C. & LEVIN, N. (1961). *J. Chem. Soc.* pp. 1224-1228.
- BLOOMFIELD, J. J. (1968a). *Tetrahedron Lett.* pp. 587-590.
- BLOOMFIELD, J. J. & MOSER, R. E. (1968b). *J. Amer. Chem. Soc.* **90**, 5625-5626.
- COLEMAN, J. K. (1975). Ph.D. Dissertation, Univ. of Oklahoma, Norman, Ok. 73069.
- DUNITZ, J. D. & SCHOMAKER, V. (1952). *J. Chem. Phys.* **20**, 1703-1707.
- FINK, R., VAN DER HELM, D. & NEELY, S. C. (1975). *Acta Cryst.* **B31**, 1299-1303.
- GROOT, A. DE, OUDMAN, D. & WYNBERG, H. (1969). *Tetrahedron Lett.* **20**, 1529-1531.
- HEINE, H. (1971). *Chem. Ber.* **194**, 2869-2872.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202, 214. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
- LEONARD, N. J. & MADER, P. M. (1950). *J. Amer. Chem. Soc.* **72**, 5388-5397.
- NAGAKARA, S. & KUBOYANA, A. (1954). *J. Amer. Chem. Soc.* **76**, 1003-1005.
- NEELY, S. C., FINK, R., VAN DER HELM, D. & BLOOMFIELD, J. J. (1971). *J. Amer. Chem. Soc.* **93**, 4903-4905.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, p. 260. Ithaca: Cornell Univ. Press.
- RATHJENS, W. D., FREEMAN, N. K., GUINN, W. D. & PITZER, K. S. (1953). *J. Amer. Chem. Soc.* **75**, 5634-5642.
- REID, K. F. (1968). *Properties and Reactions of Bonds in Organic Molecules*, p. 349. New York: Elsevier.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* **B24**, 63-76.
- SHIRRELL, C. D. & WILLIAMS, D. E. (1973). *Acta Cryst.* **B29**, 1648-1653.
- SHIRRELL, D. C. & WILLIAMS, D. E. (1974a). *Acta Cryst.* **B30**, 1974-1978.
- SHIRRELL, C. D. & WILLIAMS, D. E. (1974b). *Acta Cryst.* **B30**, 245-246.
- STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175-3187.
- SUTTON, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement*, p. 514. London: The Chemical Society.
- VAN DER HELM, D. & NICHOLAS, H. B. (1970). *Acta Cryst.* **B26**, 1858-1866.