

Crystal Structure of Dimethylfulvene*

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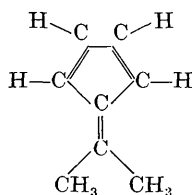
The crystal structure of dimethylfulvene has been determined at -50°C . The crystal system is monoclinic; the space group is $C2/c$, with four molecules per unit cell;

$$a = 12.07, b = 8.36, c = 7.27 \text{ \AA}, \beta = 111.5^{\circ}.$$

Molecular parameters have been determined by Fourier and least-squares refinements of 3 dimensional data.

The five membered ring is coplanar; the methyl carbon atoms are only 0.035 \AA out of that plane. The two double bonds in the ring are 1.346 \AA long; the double bond outside the ring is 1.343 \AA long; single bonds in the ring are 1.439 and 1.435 \AA long; the single C-C bonds to the methyl groups are 1.520 \AA long. The average standard deviation of bond lengths is 0.011 \AA .

An interesting system of conjugated single and double bonds is present in the dimethylfulvene molecule,



This investigation was undertaken primarily to determine the effect of the conjugation on the relative lengths of the single and double carbon to carbon bonds.

Experimental

Dimethylfulvene melts at 1.4°C . (Craig, 1954). X-ray diffraction measurements were made at $-50 \pm 5^{\circ}\text{C}$. Single crystals were grown, oriented and maintained at this temperature using standard techniques (Post, Schwartz & Fankuchen, 1951). Crystals were grown in thin-walled glass capillary tubes (0.3 mm . i.d.). They invariably grew along what was later designated as the c axis of the unit cell. The crystal system is monoclinic:

$$a = 12.07 \pm 0.03, b = 8.36 \pm 0.02, c = 7.27 \pm 0.02 \text{ \AA}; \\ \beta = 111.5 \pm 0.5^{\circ}.$$

Unit-cell dimensions were computed from single crystal photographs taken with a precession camera whose camera constant had been calibrated using sodium chloride as a standard. There are four molecules in the unit cell.

Twinning of the crystals, with the bc face common

to both twins, was of frequent occurrence. The twinning was detected on $(h0l)$ precession and on $(hkl0)$ Weissenberg photographs. The nature of the twinning became clearer as details of the crystal structure were uncovered. The molecule is essentially flat, with its molecular axis parallel to b . The normal to the molecular plane is inclined about 8° to c . Rotation of molecules by 16° about b would lead to the type of twinning observed.

Crystals suitable for X-ray diffraction study could be obtained only after careful vacuum distillation of the starting material. Full data in three dimensions were obtained from the following photographs:

Precession: $h0l, h1l, 0kl$ (Mo K radiation).

Weissenberg: $hk0$ through $hk5$ (Cu K radiation).

Altogether 453 independent reflections were used in the analysis, including 51 unobserved reflections which were included at half the appropriate minimum observable values.

Intensities were estimated visually, using calibrated intensity strips. The usual Lorentz and polarization corrections were applied. Absorption corrections were considered unnecessary.

Systematic absences indicated that the space group is either Cc or $C2/c$. In $C2/c$, symmetry axes of the four molecules must coincide with the four twofold axes of the unit cell. A Patterson ($h0l$) projection indicated that the molecule was approximately flat, with its plane inclined about 98° to c , and with its molecular axis parallel to b , as required by $C2/c$. The choice of $C2/c$ as the more probable space group was strengthened by a chance comparison of $(h0l)$ precession photographs of dimethylfulvene and ethylene carbonate. The intensity distributions in the two photographs are strikingly similar. The space group of ethylene carbonate is $C2/c$ (Brown, 1954). The projection of that molecule down its axis would be expected to resemble greatly the corresponding projection of

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dimethylfulvene. The similarity between the two photographs indicated the likelihood of similar molecular packing in the two cases. Our choice of $C2/c$ was, of course, confirmed during the course of the structure analysis.

Structure determination

If the space group is actually $C2/c$, and if the shape and size of the dimethylfulvene molecule, as well as its approximate inclination relative to the c axis, are assumed, the determination of the structure is reduced to a one parameter problem: the determination of the y positional coordinate of an atom in one of the four fold positions ($4e$) of $C2/c$. (This position is referred to below as y_0 .)

As a first approximation the molecule was assumed to be perfectly flat with single and double bond lengths of 1.47 and 1.37 Å respectively. Approximate values of y_0 were deduced in two ways. The first method was based on the analysis of the Patterson ($OV\frac{1}{2}$) section; it yielded a value of $y_0=0.138$. The second procedure involved comparing the intense (021) and (11 $\bar{1}$) reflections with the still more intense (002) reflection. The ratio $F_0(002)/F_0(021)$ is 2.0. That ratio was computed for different values of y_0 ; the minimum calculated value of that ratio was 2.4 for $y_0=0.093$ and 0.157. In this calculation, and in the one outlined below, it was assumed that the (002) reflection received full contributions from all the carbon atoms: the Patterson ($h0l$) projection had indicated that this was approximately correct.

The twofold ambiguity in y_0 results from the even character of the k index in (021). The ambiguity was eliminated by a similar calculation of the ratio $F(002)/F(11\bar{1})$. The observed ratio is 2.2 and the calculated value was 2.1 for $y_0=0.157$ and 3.9 for

$y_0=-0.093$. It was clear that 0.157 was the better choice of the two based on its agreement with the value (0.138) deduced from the Patterson ($OV\frac{1}{2}$) section. $y_0=0.138$ was used as the starting point for subsequent calculations. Intensities were first normalized using Wilson's method, which also yielded a value of $B=3.46$ Å² for the temperature factor.

The following electron density maps were computed and refined in the usual way: projection down the c axis; a bounded projection from 0 to $\frac{1}{2}$ down the c axis; and, a line synthesis along $(0, y, \frac{1}{4})$.

In addition, the half-cell bounded projection down the c axis, and the $0, y, \frac{1}{4}$ line synthesis, were computed using calculated structure factors and positional parameters derived from previous electron density calculations. The z parameters of carbon atoms 3, 4 and 5 were determined from electron density line syntheses, using the previously established x and y parameters of the atoms. Positional parameters of atoms computed from these syntheses are shown in Table 1.

A slight improvement in R resulted from the application of back shift corrections to the positional parameters; for observed reflections only, $R_{(hkl)}$ decreased from 28.1 to 26.7%. When unobserved reflections were included in the calculations, the corresponding values of R were 30.8 and 30.1%.

An effort was then made to refine the structure by least-squares calculations using the IBM NYXRI program (Friedlander *et al.*, 1955). In this program, individual isotropic temperature factors are assigned to the carbon atoms and these were refined together with the positional parameters of the atoms. The temperature factor of the hydrogen atoms was fixed at $B=4$. Six cycles of refinement led to the positional parameters listed in Table 1. $R_{(hkl)}$ fell to 22.4%, in

Table 1. Refinement of position coordinates

Atom		A_1	A_2	A_3	A_4	B	C	D	
		$\int_0^1 \rho(x, y, z) dz$	$\int_0^{\frac{1}{2}} \rho(x, y, z) dz$	$\rho(0, y, \frac{1}{4})$	$\rho(x_c Y_c Z)$			Isotropic least squares	Fourier calcs. based on B
								Cycle 15	Cycle 16
C ₁	y	0.1390	0.1368	0.1368	—	0.1397	0.1400	0.14163	0.14153 ± 0.00089
C ₂	y	—	-0.0163	-0.0165	—	-0.0203	-0.01983	-0.01923	-0.01923 ± 0.00102
C ₃	x	0.1012	0.1030	—	—	0.1020	0.1017	0.10141	0.10142 ± 0.00053
	y	0.2410	0.2410	—	—	0.2461	0.2452	0.24477	0.24475 ± 0.00082
	z	—	—	—	0.2883	0.2883	0.2882	0.28769	0.28773 ± 0.00106
C ₄	x	0.0655	0.0660	—	—	0.0648	0.0650	0.06327	0.06319 ± 0.00067
	y	0.3950	0.4003	—	—	0.3966	0.3970	0.39714	0.39714 ± 0.00074
	z	—	—	—	0.2756	0.2756	0.2752	0.27393	0.27387 ± 0.00115
C ₅	x	0.1122	0.1122	—	—	0.1096	0.1112	0.11228	0.11205 ± 0.00064
	y	-0.1238	-0.1187	—	—	-0.1170	-0.1218	-0.11918	-0.11933 ± 0.00081
	z	—	—	—	0.2962	0.2960	0.2962	0.29601	0.29585 ± 0.00110
H ₃								$\begin{cases} x & 0.196 \pm 0.004 \\ y & 0.219 \pm 0.006 \\ z & 0.314 \pm 0.009 \end{cases}$	
H ₄								$\begin{cases} x & 0.118 \pm 0.006 \\ y & 0.505 \pm 0.010 \\ z & 0.300 \pm 0.009 \end{cases}$	

the course of these calculations (all reflections, including 'unobserved', were used). It was felt that improvement in the agreement between F_o and F_c and, more important, in the molecular parameters should result from additional least-squares refinements using anisotropic temperature factors for individual atoms. Such calculations have been carried out for us by Prof. W. N. Lipscomb and his staff. The computing program has been described elsewhere (Rossman *et al.*, 1959).

In this program the function minimized is $E = wk^2(F_o^2 - F_c^2)^2$, where w is the weighting factor applied to the scaled F_o and k is the scale factor. w was taken as 1 for $F_o \leq 4F_{\min.}$ and as $(4F_{\min.}/F_o)^4$ for $|F_o| \geq 4F_{\min.}$. For these calculations $F_{\min.}$ was assumed to equal 4. The usefulness of the weighting scheme was demonstrated by computed four unweighted least-squares cycles. The calculated standard deviation of the parameters was approximately three times as large as the standard deviations computed on the basis of four weighted least-squares cycles.

Sixteen cycles of least-square refinements (weighted) were computed, although only minor changes in atomic coordinates and in R occurred after the sixth cycle. Between the sixth and final cycles, R fell from 16.8% to a final value of 15.2% for all 453 reflections (including unobserved).

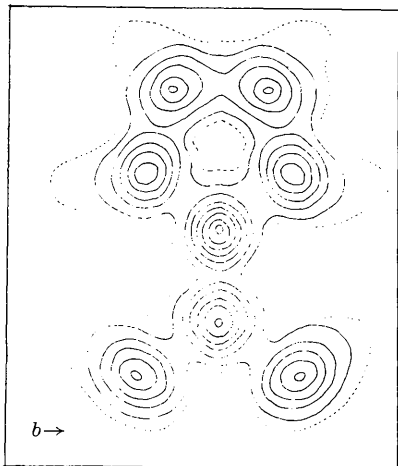


Fig. 1. Electron-density section in molecular plane.

This value still seemed rather high. It was attributed, in part, to two factors. First, it had been observed early in the refinement that the methyl hydrogen atoms were acquiring extremely high temperature factors (up to $B=30$). It was felt that these hydrogen atoms might be disordered and they were therefore omitted from subsequent calculations with, presumably, adverse effects on R . Much more important was the effect of extinction. Four ($h0l$) reflections, (200), (002), (202) and $(20\bar{2})$ clearly suffered strongly from this cause. Their omission from the calculations caused R to decrease to 12.5% (including

unobserved reflections). It was not considered worthwhile to try to correct other reflections systematically for extinction. The weighting scheme used made it unlikely that the application of the indicated changes in the magnitudes of these F 's would affect atomic coordinates appreciably. Positional parameters computed in the 15th and 16th least-squares refinement cycles are also shown in Table 1. Changes in positional coordinates of carbon atoms, except for carbon 5, were gratifyingly small. The average change in the

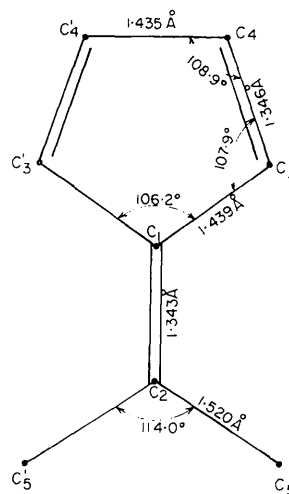


Fig. 2. Bond lengths and angles in dimethylfulvene.

positional coordinates of carbon atoms 1, 2, 3 and 4 between the 15th and 16th cycles was 0.00034 Å. It was considerably higher in the case of C_5 where the average change was 0.0018 Å.

Electron density sections, based on signs of coefficients determined in the least-squares calculations, were computed at intervals of $Z/40$. A map of the electron density in the 'best' plane through the molecule, is shown in Fig. 1. A schematic diagram of the molecule, listing bond lengths and angles, is shown in Fig. 2.

Discussion

The progress of the refinement of the molecular parameters is shown in Tables 1 and 2. The best plane through carbon atoms 1, 2, 3, 3', 4 and 4' passes within 0.002 Å of all these atoms. The five membered ring and the attached double bond are therefore coplanar, within experimental error. Atom C_5 is 0.035 Å out of the plane of the other atoms. In view of the consistently high positional uncertainty associated with this atom, this is of doubtful physical significance; in any event, the deviation of this atom from the best plane of the others, even if real, is very small and we may describe the entire molecule, except for the methyl hydrogen atoms, as essentially planar.

Temperature factors computed for the carbon atoms and the two hydrogen atoms on the five membered

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Refinement of the Structure of *n*-Nonanoic Acid Hydrazide*

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The crystal structure of *n*-nonanoic acid hydrazide has been refined by three-dimensional ΔF syntheses. The structure consists of molecular ribbons laced together by N-H \cdots O and N-H \cdots N bonds. These ribbons laid face-to-face make up 'molecular double layers' similar to those occurring in many other long-chain structures.

Within the limit of experimental error, the paraffin chain is planar except for a small deviation at the methyl C atom, and the C-C bonds are equal except for that adjacent to the carbonyl group. The average C-C bond length when corrected for angular oscillation is 1.526 Å. Although the maximum corrections in the bond lengths due to angular oscillation of the molecule as a whole are small, it is shown that similar corrections due to oscillation of an atom about another to which it is bonded may be relatively large. Thus the correction to the C-O bond is +0.014 Å or three times its standard deviation.

It has been shown that the melting points of monoacyl derivatives of hydrazine with 4-12 carbon atoms fall on a single smooth curve when plotted against the number of carbon atoms (Kyame, Fisher & Bickford, 1947). This implies that the compounds with even or odd numbers of carbon atoms in the chain have either the same structure or different structures with similar lattice energies and variation of lattice energies with number of carbon atoms.

The length of the C-C single bonds in organic molecules is usually taken to be equal to that in diamond, 1.5445 Å, although until recently this has not been subject to experimental verification with any degree of precision. Furthermore, the C-C bonds in hexamethylene diamine indicate a possible alternation in length (Binnie & Robertson, 1950).

Finally, certain paraffin chain compounds are good models of biological membrane systems and their structures shed light on possible chain configuration and packing in such systems.

For these reasons, the structures of two monoacyl hydrazides have been determined, one with an even number (Jensen, 1956), the other with an odd number of C atoms in the chain. This is to report the structure

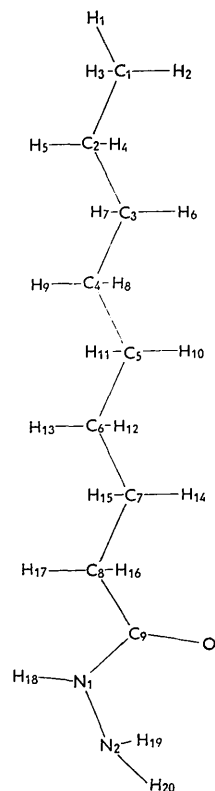


Fig. 1. Structural formula for *n*-nonanoic acid hydrazide.

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