

The Crystal and Molecular Structure of Dicinnamyl Disulphide

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(Received 31 December 1970)

The crystal and molecular structure of dicinnamyl disulphide has been determined from X-ray data by Patterson techniques. The structure has been refined by block-diagonal least-squares and difference Fourier syntheses on three-dimensional data. The unit cell is orthorhombic, space group $Fdd2$, with $a = 17.42$, $b = 34.18$, $c = 5.42$ Å, and contains eight molecules. The final R value based on 660 observed reflexions is 9.5%. A twofold axis of symmetry passes through the mid point of the S–S bond. The central part of the molecule C–S–S–C adopts a skewed non-planar configuration similar to hydrogen peroxide and a number of other disulphides. The S–S bond of 2.01 Å is short and possesses 25% double bond character. The dihedral angle of 66.4° differs from the usual angle of about 90°, and the S–C bond length of 1.88 Å is very significantly long. It is suggested that a bifurcated intramolecular hydrogen bond is formed by a methylene hydrogen atom attached to C(3) with both sulphur atoms, with a similar hydrogen bond arrangement from C(3'). This could account for the convoluted nature of the molecule and the unusual dihedral angle and bond lengths.

Introduction

The crystal structure of dicinnamyl disulphide $C_6H_5 \cdot CH:CH \cdot CH_2 \cdot S \cdot S \cdot CH_2 \cdot CH:CH \cdot C_6H_5$ was undertaken as part of a series of structural studies on disulphides to see the effect of the conjugated double bond or steric factors on the lengths of the S–S and C–S bonds. A preliminary two-dimensional structure had previously been published (Smith & Whyman, 1964), and we are grateful to Mr G. W. Smith (BP Research Centre, Sunbury on Thames) for providing a sample and for unpublished information.

Experimental

Crystals were in the form of thin colourless needles elongated along c . Most of the needles were found to be aggregates of many thinner crystals joined face to face, but eventually a single crystal $0.3 \times 0.1 \times 0.1$ mm was obtained, and this gave straight extinction. Equi-inclination Weissenberg data were collected photographically and measured visually for the layers $hk0$ to $hk4$. Lorentz and polarization corrections were applied but no corrections were made for absorption or extinction.

Crystal data

$(C_9H_9S)_2$, $M = 298.46$

Orthorhombic $a = 17.42$, $b = 34.18$, $c = 5.42$ Å,

all ± 0.02 Å

$U = 3227.2$ Å³, $F_{000} = 1264$, $\lambda(\text{Cu } K\alpha) = 1.5418$ Å, $\mu = 27.7$ cm⁻¹, $Z = 8$,

$D_c = 1.228$ g.cm⁻³, $D_m = 1.23$ g.cm⁻³ (by flotation in aqueous potassium iodide)

Reflexions present only when

$hkl: h+k, k+l, (h+l) = 2n$;

$0kl: k+l = 4n$ ($k, l = 2n$);

$h0l: h+l = 4n$, ($h, l = 2n$);

$hk0: (h, k = 2n)$; $h00: (h = 4n)$;

$0k0: (k = 4n)$; $00l: (l = 4n)$.

These absences uniquely determine the space group as $Fdd2$.

Structure analysis

A Patterson summation sharpened to point sulphur atoms at rest was performed on the $hk0$ data, and gave a trial structure similar to the two-dimensional structure previously published (Smith & Whyman, 1964). Structure factor and preliminary least-squares refinement with unit weights rapidly reduced R to 18.1% using atomic scattering factors due to Hanson, Herman, Lea & Skillman (1964) with both real and imaginary corrections for anomalous dispersion (Dauben & Templeton, 1955) applied to the sulphur atoms.

Using three-dimensional data, Patterson, sharpened Patterson and heavy atom Fourier (based on sulphur atoms) summations were performed to resolve ambiguities in the three-dimensional structure. The z/c coordinate for the heaviest atom (sulphur) was fixed to define the origin, and this model gave a value of $R = 28.1\%$. A full-matrix least-squares program which would handle this space group was not available so refinement was carried out by block-diagonal least-squares and difference Fourier techniques using the X-ray 63 system due to Professor J. M. Stewart (University of Maryland) as adapted for the SRC Chilton Atlas computer by Dr J. C. Baldwin. When R had decreased to 11.1%, possible hydrogen atom peaks were apparent on difference Fourier synthesis. Positions of hydrogen atoms were calculated at a distance of 1.075 Å from the carbon atoms to which they are attached, and these were included in fixed positions

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with a temperature factor of $B=9.0 \text{ \AA}^2$ in subsequent calculations. The weighting scheme used was a Cruickshank type

$$w = \frac{1}{A + B|F_o| + |CF_o^2|}$$

Table 1. Final positional parameters and e.s.d.'s

	x/a	y/b	z/c
S	0.0174 (3)	0.0280 (1)	0.0000
C(1)	0.0797 (11)	0.0312 (5)	-0.2827 (57)
C(2)	0.1421 (13)	-0.0003 (6)	-0.2475 (66)
C(3)	0.1458 (12)	-0.0230 (5)	-0.0486 (59)
C(4)	0.2003 (8)	-0.0589 (4)	-0.0285 (43)
C(5)	0.2584 (8)	-0.0640 (4)	-0.2017 (45)
C(6)	0.3058 (11)	-0.0965 (6)	-0.1893 (61)
C(7)	0.2998 (7)	-0.1226 (7)	0.0052 (62)
C(8)	0.2469 (10)	-0.1158 (5)	0.1914 (52)
C(9)	0.1980 (11)	-0.0842 (5)	0.1723 (52)

Table 2. Calculated hydrogen positions

	Bonded to	x/a	y/b	z/c
H(1)	C(1)	0.0465	0.0254	-0.4459
H(11)	C(1)	0.1052	0.0598	-0.2969
H(2)	C(2)	0.1844	-0.0041	-0.3899
H(3)	C(3)	0.1094	-0.0162	0.1058
H(5)	C(5)	0.2665	-0.0426	-0.3451
H(6)	C(6)	0.3476	-0.1015	-0.3318
H(7)	C(7)	0.3360	-0.1481	0.0118
H(8)	C(8)	0.2441	-0.1348	0.3488
H(9)	C(9)	0.1570	-0.0789	0.3168

with values of $A=0.9174$, $B=-0.0141$ and $C=0.0139$.

The final R value was 9.5%. Results are listed in Tables 1-8.

Table 3. Final temperature factor parameters

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
S	5.37	5.37	7.08	-0.25	-0.01	0.18

The form of the anisotropic temperature factor used is

$$TF = \exp \left[-\frac{1}{4}(h^2 a^2 B_{11} + k^2 b^2 B_{22} + l^2 c^2 B_{33} + 2hka^* b^* B_{12} + 2hla^* c^* B_{13} + 2klb^* c^* B_{23}) \right]$$

B (isotropic)

C(1)	7.27	C(6)	7.89
C(2)	8.48	C(7)	8.50
C(3)	7.98	C(8)	7.37
C(4)	6.15	C(9)	6.34
C(5)	6.33		

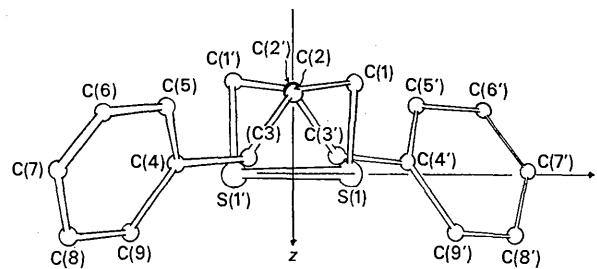


Fig. 1. A view of the molecule.

Table 4. Observed and calculated structure amplitudes

h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c	h	k	l	F _o	F _c
4	0	0	261.9	232.0	12	0	0	17.8	15.6	6	38	0	18.5	16.8	19	13	1	5.3	6.2
8	0	0	45.9	48.5	12	0	0	17.7	18.2	6	38	0	18.5	16.8	21	13	1	5.7	5.9
12	0	0	12.5	16.3	16	0	0	9.8	9.2	4	40	0	14.5	14.3	23	13	1	6.1	6.0
4	2	0	27.1	31.4	2	18	0	158.5	159.1	8	40	0	4.1	4.4	5	15	1	24.3	24.3
8	2	0	128.7	125.0	6	18	0	9.7	9.3	4	42	0	4.1	4.2	7	15	1	65.0	77.7
2	0	12	8.2	12.8	2	18	0	87.8	75.1	7	1	1	97.1	88.0	10	15	1	47.6	43.4
10	2	0	32.7	30.4	10	18	0	38.2	41.3	9	1	1	42.7	39.1	11	15	1	29.2	28.6
12	2	0	28.5	24.4	16	18	0	3.6	6.5	11	1	1	6.7	12.3	15	1	1	24.1	20.5
14	2	0	23.1	19.9	20	18	0	127.5	114.3	13	1	1	21.1	26.6	15	15	1	21.5	23.2
18	2	0	19.7	26.3	22	18	0	24.0	23.6	15	1	1	5.6	5.4	17	15	1	9.4	11.2
20	2	0	101.8	92.5	24	18	0	9.5	6.7	17	1	1	60.0	73.2	19	15	1	5.7	7.5
8	4	0	110.5	102.7	6	20	0	10.2	13.3	19	1	1	7.8	7.7	21	15	1	5.1	4.6
10	4	0	46.8	47.6	10	20	0	44.7	38.8	21	1	1	7.4	8.3	23	1	1	63.4	70.4
12	4	0	23.7	22.9	14	20	0	22.8	17.2	9	2	1	75.4	73.8	7	17	1	30.1	31.4
14	4	0	48.7	58.2	18	20	0	10.1	10.1	9	2	1	23.2	15.2	11	1	1	9.0	9.7
16	4	0	22.6	39.4	22	20	0	35.3	41.2	15	2	1	18.6	19.4	17	1	1	6.9	7.9
18	4	0	20.2	26.3	26	20	0	25.4	32.5	19	2	1	12.5	12.4	21	1	1	7.2	6.9
2	6	0	352.0	321.0	8	22	0	25.4	32.5	17	2	1	11.2	11.8	19	1	1	5.0	4.3
4	6	0	254.6	273.8	10	22	0	15.6	16.9	19	2	1	4.5	4.3	21	1	1	3.9	1.9
6	6	0	88.0	85.6	12	22	0	54.8	23.5	21	2	1	44.9	46.5	23	1	1	17.0	14.3
8	6	0	35.9	53.1	14	22	0	40.4	39.9	24	2	1	45.6	45.5	25	1	1	6.5	6.8
10	6	0	31.1	34.3	16	22	0	27.7	29.6	26	2	1	105.2	99.9	27	1	1	68.9	52.8
12	6	0	24.5	20.8	18	22	0	23.1	22.3	28	2	1	80.6	80.1	29	1	1	15.4	17.3
14	6	0	96.6	112.1	20	22	0	39.3	34.1	30	2	1	41.8	39.8	31	1	1	12.5	14.6
2	8	0	24.0	27.3	22	24	0	45.5	36.5	32	2	1	28.2	29.1	33	1	1	7.7	6.0
4	8	0	53.9	50.8	24	24	0	28.1	23.7	34	2	1	19.8	19.6	35	1	1	4.1	3.9
6	8	0	102.6	116.1	26	24	0	21.7	25.5	36	2	1	6.8	8.9	37	1	1	1.9	1.1
8	8	0	43.7	40.9	28	24	0	8.4	8.6	38	2	1	16.0	16.3	39	1	1	30.4	31.8
10	8	0	62.8	56.6	30	24	0	1.9	1.4	40	2	1	2.21	2.0	41	1	1	48.2	48.3
12	8	0	4.5	5.4	32	24	0	1.9	1.4	42	2	1	46.2	46.6	43	2	1	170.7	195.4
14	8	0	41.7	53.8	34	24	0	36.9	30.0	44	2	1	68.0	62.1	45	2	1	26.8	26.8
16	8	0	22.2	24.7	36	24	0	11.8	14.7	46	2	1	47.2	48.9	47	2	1	65.9	63.7
2	10	0	79.8	80.1	38	24	0	20.1	22.3	48	2	1	49.8	49.1	49	2	1	8.3	9.1
4	10	0	38.5	39.4	40	24	0	9.3	9.3	50	2	1	36.8	37.6	51	2	1	5.3	5.1
6	10	0	48.1	48.1	42	24	0	16.7	25.3	52	2	1	30.0	29.5	53	2	1	48.2	48.3
8	10	0	22.0	23.9	44	24	0	1.3	0.9	54	2	1	16.2	21.4	55	2	1	15.2	23.5
10	10	0	10.8	10.8	46	24	0	28.1	23.7	56	2	1	40.7	37.2	57	2	1	4.0	3.7
12	10	0	78.6	90.2	48	24	0	0.6	1.0	58	2	1	15.2	18.5	59	2	1	3.1	3.1
14	10	0	1.1	0.8	50	24	0	15.4	16.1	60	2	1	11.4	12.3	61	2	1	20.3	20.3
16	10	0	41.3	40.3	52	24	0	2.2	2.5	62	2	1	26.5	27.1	63	2	1	12.1	12.0
2	12	0	85.8	92.8	54	24	0	31.3	34.4	64	2	1	37.0	36.7	65	2	1	19.0	20.0
4	12	0	58.9	53.3	56	24	0	18.6	18.6	66	2	1	11.9	11.9	67	2	1	20.1	15.0
6	12	0	154.7	152.3	58	24	0	22.1	23.6	68	2	1	49.1	49.0	69	2	1	12.1	12.0
8	12	0	111.6	107.6	60	24	0	9.5	11.8	70	2	1	33.2	26.7	71	2	1	5.5	6.0
10	12	0	74.1	72.5	62	24	0	21.1	21.1	72	2	1	24.6	20.4	73	2	1	27.1	23.5
12	12	0	42.4	27.7	64	24	0	1.1	0.4	74	2	1	1.9	2.4	75	2	1	27.5	26.6
14	12	0	29.5	27.6	66	24	0	20.4	28.7	76	2	1	7.4	7.9	77	2	1	25.6	29.7
16	12	0	12.9	17.3	68	24	0	17.6	18.3	78	2	1	2.1	2.4	79	2	1	15.2	15.0
2	14	0	3.6	2.2	70	24	0	9.7	10.6	80	2	1	51.1	57.2	81	2	1	27.5	27.5
4	14	0	12.0	13.1	72	24	0	15.1	16.1	82	2	1	7.1	6.8	83	2	1	10.9	11.5
6	14	0	153.0	145.8	74	24	0	22.2	25.2	84	2	1	11.8	12.4	85	2	1	17.0	15.7
8	14	0	7.6	6.8	76	24	0	68.6	55.2	86	2	1	11.1	12.6	87	2	1	10.3	10.3
10	14	0	32.1	34.4	78	24	0	7.1	6.8	88	2	1	20.3	24.1	89	2	1	3.1	3.2
12	14	0	27.4	25.6	80	24	0	13.2	14.2	90	2	1	11.8	12.4	91	2	1	10.7	11.2
14	14	0	36.7	30.7	82	24	0	7.6	10.0	92	2	1	17.1	15.6	93	2	1	25.4	22.8
16	14	0	43.2	42.0	84	24	0	10.5	10.3	94	2	1	9.9	10.4	95	2	1	15.0	15.0
2	16	0	13.9	17.7	86	24	0	12.9	15.0	96	2	1	13.1	7.6	97	2	1	14.1	15.0
4	16	0	4.9	5.8	88	24	0	13.1	15.4	98	2	1	5.7	7.1	99	2	1	17.5	19.1
6	16	0	70.8	74.9	90	24	0	36.1	34.3	100	2	1	7.3	10.8	101	2	1	8.1	7.9
8	16	0	39.8	43.4	92	24	0	5.6	3.2	102	2	1	13.1	27.5	24.2	5.2	1	16.1	18.2
10	16	0	21.7	25.2	94	24	0	16.4	16.4	104	2	1	21.7	25.2	25.2	16.4	1	20.9	20.9
12	16	0	17.1	17.1	96	24	0	8.3	9.0	106	2	1	13.1	31.2	29.3	9.2	1	17.9	19.8
14	16	0	5.3	3.3	98	24	0	19.5	23.3	108	2	1	11.3	22.9</					

Table 5. *Agreement analysis*

F_{obs}	Number of reflexions	R	$\sin \theta$	Number of reflexions	R	Zone	Number of reflexions	R
0-5	55	13.2%	0.0-0.1	0	-	hk0	137	9.1%
5-10	149	10.3	0.1-0.2	5	11.0%	hk1	157	7.9
10-15	95	8.7	0.2-0.3	12	4.4	hk2	150	9.5
15-20	76	10.2	0.3-0.4	35	7.4	hk3	127	10.8
20-25	69	12.9	0.4-0.5	53	6.6	hk4	89	10.2
25-30	47	12.9	0.5-0.6	86	10.7			
30-35	26	10.0	0.6-0.7	120	11.5			
35-40	29	9.2	0.7-0.8	130	11.8			
40-45	14	10.4	0.8-0.9	124	10.0			
45-50	18	8.3	0.9-1.0	95	8.0			
50-55	12	4.2						
55-60	6	4.8						
60-65	6	8.7						
65-70	7	9.9						
70-75	9	7.9						
75-80	5	6.5						
80-85	5	9.1						
85-90	4	6.1						
90-95	3	8.7						
> 95	25	7.5						

Table 6. *Bond lengths (Å) and their estimated standard deviations*

Bond	Distance
S—S'	2.008 (7)
S—C(1)	1.88 (3)
C(1)—C(2)	1.54 (3)
C(2)—C(3)	1.33 (4)
C(3)—C(4)	1.55 (2)
C(4)—C(5)	1.39 (3)
C(5)—C(6)	1.39 (2)
C(6)—C(7)	1.39 (4)
C(7)—C(8)	1.39 (4)
C(8)—C(9)	1.38 (3)
C(9)—C(4)	1.39 (3)

Discussion

A view of the molecule is shown in Fig. 1. The two halves of the molecule are related by a twofold axis of symmetry.

The z/c coordinate for S(1) was fixed to define the origin and consequently has no error. Strictly the standard deviations of the other atoms should be increased accordingly, but the X-ray 63 programs do not do this. To obtain a better estimate of the errors in bond lengths and angles involving S(1) an estimated standard deviation of 0.0012 was assumed for the z/c coordinate. The standard deviations of the S—S bond and the angle C(1)—S(1)—S(1') were calculated differently from the others to allow for the twofold axis (Cruickshank & Robertson, 1953).

The S—S bond length of 2.01 Å is considerably shorter than the Pauling (1960) single bond value of 2.08 Å, and using Pauling's relationship the bond may be ascribed 25% double-bond character. The observed bond length is slightly shorter than the value of 2.02 Å in dibenzyl disulphide (Lee & Bryant, 1969*a*), 2.03 Å in diphenyl disulphide (Lee & Bryant, 1969*b*) and considerably shorter than the value of 2.06 Å in 2,2'-diaminodiphenyl disulphide (Lee & Bryant, 1970).

Table 7. *Bond angles (°) and their estimated standard deviations*

Bond	Angle
S'—S—C(1)	103.3 (0.8)
S—C(1)—C(2)	105.4 (1.6)
C(1)—C(2)—C(3)	122.8 (2.3)
C(2)—C(3)—C(4)	123.2 (2.2)
C(3)—C(4)—C(5)	119.6 (1.7)
C(3)—C(4)—C(9)	121.8 (1.7)
C(5)—C(4)—C(9)	118.2 (1.7)
C(4)—C(5)—C(6)	120.0 (1.8)
C(5)—C(6)—C(7)	120.6 (2.2)
C(6)—C(7)—C(8)	119.6 (2.3)
C(7)—C(8)—C(9)	119.3 (2.1)
C(8)—C(9)—C(4)	121.8 (2.0)

Table 8. *Intramolecular close approaches*

S(1)···C(2)	2.73 Å	C(1)···H(2)	2.26 Å
S(1)···C(3)	2.85	C(1)···H(3)	2.71
S(1)···C(3')	2.86	C(2)···H(1)	2.17
S(1)···C(2')	3.23	C(2)···H(11)	2.17
S(1)···C(1')	3.05	C(2)···H(3)	2.07
S(1)···H(1)	2.47	C(2)···H(5)	2.66
S(1)···H(11)	2.47	C(3)···H(2)	2.07
S(1)···H(3)	2.28	C(3)···H(5)	2.73
S(1)···H(3')	2.32	C(3)···H(9)	2.76
C(1)···C(3)	2.53	C(4)···H(2)	2.73
C(2)···C(4)	2.54	C(4)···H(3)	2.27
C(2)···C(5)	2.98	C(4)···H(5)	2.14
C(3)···C(5)	2.55	C(4)···H(9)	2.13
C(3)···C(9)	2.58	C(5)···H(2)	2.62
C(4)···C(6)	2.41	C(5)···H(6)	2.14
C(4)···C(7)	2.79	C(6)···H(5)	2.14
C(4)···C(8)	2.42	C(6)···H(7)	2.14
C(5)···C(7)	2.41	C(7)···H(6)	2.13
C(5)···C(8)	2.78	C(7)···H(8)	2.14
C(5)···C(9)	2.39	C(8)···H(7)	2.14
C(6)···C(8)	2.40	C(8)···H(9)	2.12
C(6)···C(9)	2.75	C(9)···H(3)	2.81
C(7)···C(9)	2.39	C(9)···H(8)	2.14
C(1)···C(1')	3.50		

The central part of the molecule C-S-S-C adopts a skewed non-planar configuration similar to H₂O₂ (Abrahams, Collins & Lipscomb, 1951) and a number of other disulphides. The dihedral angle between the planes through C(1), S(1), S(1') and C(1'), S(1'), S(1) is 66.4°, and differs from the values of 96.2° in diphenyl disulphide, 92.1° in dibenzyl disulphide and 90.5° in 2,2'-diamino diphenyl disulphide. Hordvik (1966) suggests that a dihedral angle of 90° gives the optimum π overlap of orbitals. Contrary to this explanation dicinnamyl disulphide has the shortest S-S bond length and the greatest deviation of dihedral angle from 90°.

The observed S-C(1) distance of 1.88 Å is very significantly long compared with the average distance of 1.81₅ Å found in 11 compounds by Cox & Jeffrey (1951), 1.81 and 1.79 Å in diphenyl disulphide, 1.84 and 1.85 Å in dibenzyl disulphide and 1.77 and 1.75 Å in 2,2'-diaminodiphenyl disulphide.

The bond angle S(1)-C(1)-C(2) of 105.4° is slightly distorted from the normal tetrahedral value, and the angles C(1)-C(2)-C(3) and C(2)-C(3)-C(4) of 122.8 and 123.2° from the expected plane trigonal arrangement. The lengths C(1)-C(2) and C(3)-C(4) of 1.54 and 1.55 Å are normal for an aliphatic single bond and the distance C(2)-C(3) of 1.33 Å is close to the usual double-bond value of 1.34 Å. The distances and angles in the benzene rings are all normal. The equations to the planes through the two benzene rings calculated by the method of Schomaker, Waser, Marsh & Bergman (1959) are

$$11.37X + 18.99Y + 2.79Z = 1.12$$

and

$$11.37X + 18.99Y - 2.79Z = 1.12$$

where X , Y and Z refer to the real unit cell axes.

The deviations of the atoms from the plane are C(4) = 0.043 Å, C(5) = -0.039 Å, C(6) = 0.005 Å, C(7) = 0.026 Å, C(8) = -0.022 Å, C(9) = -0.012 Å, and the angle between these two planes is 62.0°.

There are no intermolecular approaches less than the sum of the van der Waals radii, but there are a number of close approaches within one molecule and these are listed in Table 8. A number of these involve unavoidable C...C contacts, for example across a benzene ring. Though the S(1)...C(2) distance is very short, it is

not involved in hydrogen bonding. The four contacts S(1)...C(3), S(1)...C(3'), S(1')...C(3) and S(1')...C(3') of 2.85-2.86 Å are also particularly short. The S(1)...H(3) and S(1')...H(3) distances of 2.28 and 2.32 Å respectively are extremely short. The combined evidence suggests the possibility that H(3) is hydrogen bonded to both S(1) and S(1'), and similarly H(3') is hydrogen bonded to S(1) and S(1'). The angles C(3)-H(3)...S(1) and C(3)-H(3)...S(1') are 109 and 111° respectively. Hydrogen bonds are strongest if the angle at hydrogen is 180°. It would be expected that a bifurcated hydrogen bond between three heavier atoms would be strongest with an angle of 120° at hydrogen. The postulated bifurcated hydrogen bonds could account for the convoluted nature of the molecule and the reduced dihedral angle.

Our thanks are due to Mrs J. M. Thomas (SRC Atlas Computer Laboratory) for assistance with computing, to the Science Research Council for equipment grants, and to the British Petroleum Company for a research studentship to MWRB.

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