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N,N'-Bis-(2,2,6,6-tetramethylpiperidyl-4)-succinic acid Diamide Dihydrate*

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$C_{22}H_{42}O_2N_4.2H_2O$: monoclinic, space group $P2_1/c$, $a=13{\cdot}069$ (6), $b=13{\cdot}029$ (6), $c=15{\cdot}658$ (6) Å, $\beta=99{\cdot}96$ (5)°, $Z=4$, $d_x=1{\cdot}09$ g cm^{-3}. The unit cell contains two crystallographically different molecules, each of which is on a center of symmetry. Both molecules are fully extended, with the rings in chair conformations, but the conformation of hydrogen atoms at the terminal nitrogen atoms is different.

Introduction

The title compound was synthesized by Joss & Calvin (1972). A colorless crystal fragment approximately 0·04 cm in diameter was glued to a Pyrex fiber, and used for the measurement of 5649 data, including standards and extinctions, with a Picker FACS-I automatic diffractometer system. The observed extinctions were those unique to $P2_1/c$. Graphite-monochromated Cu $K\alpha$ ($\lambda=1{\cdot}54051$ Å for $K\alpha_1$) X-rays were used in the collection of the data by a θ–2θ scan technique using a scintillation counter. No absorption correction was deemed necessary, $\mu=6{\cdot}0$ cm^{-1} and $\mu R\sim 0{\cdot}1$. All of the reflections within the quarter sphere of reflection out to a 2θ angle of 124·5° were collected, yielding 4160 unique data of which 3767 were greater than their estimated standard deviation. Standard deviations were estimated as described by St. Clair, Zalkin & Templeton (1971), with $(0{\cdot}05I)^2$ as the additional term in $[\sigma(I)]^2$.

The positions of all the non-hydrogen atoms, including two unexpected water molecules, were obtained from an E map phased by the application of 'direct' methods. Hydrogen positions were calculated from the known chemical geometry. Full-matrix least-squares refinements were performed on all of the positional, anisotropic thermal (for the heavy atoms), and isotropic thermal (hydrogen atoms) parameters. As the number of parameters would produce a matrix that exceeds the capacity of our computer, we alternately refined half of the structure at a time. For the final refinements, all of the heavy atom parameters were refined jointly with the hydrogen atoms fixed; this was followed with a refinement of all the hydrogen atoms with the heavy atoms fixed. The final shifts were less than 0·2 and 8% of an estimated standard deviation for the heavy atoms and hydrogen parameters respectively. The weights were $1/\sigma^2(F)$, or zero if $F<\sigma(F)$. An empirical correction for extinction was applied which increased F about 10% for the strongest reflection. The final R value, $R=\sum|\Delta F|/\sum|F_o|$, for all of the reflections was 0·049, and for the 3767 non-zero weighted reflections was 0·044. The weighted R value, $R_w=[\sum w(\Delta F)^2/\sum wF_o^2]^{1/2}$, was 0·065. The goodness of fit was 1·93. Atomic form factors for spherical hydrogen were those of Stewart, Davidson & Simpson (1965) and for other atoms those of Cromer & Waber (1965).

Final atomic parameters are given in Tables 1, 2, and 3.*

Table 1. *Positional parameters of non-hydrogen atoms* ($\times 10^4$)

	x	*y*	*z*
O(1)	9657·4 (9)	1871 (1)	308·4 (9)
O(2)	3182·7 (8)	4344·5 (8)	4581·4 (6)
O(3)	3236 (1)	1025 (1)	1390·9 (9)
O(4)	5374·4 (9)	4845 (1)	2429·7 (9)
N(1)	6173 (1)	3039 (1)	1676·9 (9)
N(2)	8322 (1)	1053 (1)	722 (1)
N(3)	1595 (1)	2427 (1)	1632·4 (8)
N(4)	3784·5 (9)	4136 (1)	3327·5 (8)
C(1)	6980 (1)	2542 (1)	2324 (1)
C(2)	7533 (1)	1665 (1)	1928 (1)
C(3)	7864 (1)	1944 (1)	1078 (1)
C(4)	6934 (1)	2322 (1)	449 (1)
C(5)	6371 (1)	3233 (1)	783 (1)
C(6)	5293 (2)	3359 (2)	218 (1)
C(7)	6984 (2)	4213 (1)	749 (2)
C(8)	6407 (2)	2090 (2)	3005 (1)
C(9)	7761 (2)	3326 (2)	2762 (1)
C(10)	9152 (1)	1087 (1)	335 (1)
C(11)	−572 (1)	4906 (1)	4935 (1)
C(12)	1854 (1)	3445 (1)	1302 (1)
C(13)	2853 (1)	3811 (1)	1877 (1)
C(14)	2798 (1)	3769 (1)	2835·5 (9)
C(15)	2552 (1)	2682 (1)	3085·1 (9)
C(16)	1524 (1)	2301 (1)	2560·2 (9)
C(17)	1401 (2)	1150 (2)	2697 (1)
C(18)	595 (1)	2831 (2)	2852 (1)
C(19)	990 (2)	4244 (2)	1244 (1)
C(20)	2060 (2)	3244 (2)	384 (1)
C(21)	3894 (1)	4422 (1)	4155·2 (9)
C(22)	4931 (1)	4900 (1)	4520·6 (9)

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* A table of calculated structure factors F, $\sigma(F)$, and ΔF has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30193 (17 pp., 1 microfiche). Copies may be obtained from the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion

The biradical of this compound, where the hydrogen atoms of the two piperidyl nitrogen atoms are replaced by oxygen radicals, has been prepared (Joss & Calvin, 1972). Stable biradicals of such compounds have been proposed as a flexible strain gauge, which when attached to a membrane or a macromolecule at two points, would deform together with the support, and transduce the strain into the interaction-dependent features of the e.s.r. spectrum (Calvin *et al.*, 1969; Ferruti *et al.*, 1970). This structure determination was undertaken to provide accurate geometrical details in anticipation of such work.

Two crystallographically different, but chemically identical, molecules are at the centers of symmetry at $(\frac{1}{2},\frac{1}{2},\frac{1}{2};\ \frac{1}{2},0,0)$ and $(0,0,0;\ 0,\frac{1}{2},\frac{1}{2})$ respectively. Interatomic distances and angles are given in Tables 4 and 5. All of the hydrogen atoms associated with oxygen and nitrogen, with the exception of H(1), are involved in hydrogen bonds (Table 6). Each of the molecules is an extended chain (Figs. 1 and 2). The

Table 2. *Anisotropic thermal parameters* (Å^2)

Anisotropic temperature factors have the form $\exp[-\frac{1}{4}(B_{11}h^2a^{*2}+\ldots+2B_{12}hka^*b^*+\ldots)]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
O(1)	4·05 (6)	4·24 (6)	7·56 (8)	−1·12 (5)	1·96 (5)	−2·13 (5)
O(2)	2·92 (4)	4·24 (5)	2·76 (4)	−0·39 (4)	0·44 (4)	−0·35 (4)
O(3)	8·6 (1)	10·1 (1)	3·75 (6)	5·50 (9)	0·99 (6)	0·20 (7)
O(4)	4·14 (6)	5·79 (7)	5·43 (6)	−0·09 (5)	1·73 (5)	−1·61 (5)
N(1)	3·50 (6)	3·47 (6)	3·54 (6)	−0·06 (5)	1·12 (5)	−0·65 (5)
N(2)	3·87 (7)	3·02 (6)	6·05 (8)	−0·41 (5)	2·03 (6)	−1·45 (5)
N(3)	3·54 (6)	3·26 (6)	2·59 (5)	−0·72 (5)	0·09 (4)	−0·32 (4)
N(4)	2·77 (5)	4·19 (6)	2·62 (5)	−0·61 (5)	0·33 (4)	−0·95 (4)
C(1)	4·49 (8)	3·33 (7)	3·01 (7)	0·19 (6)	0·92 (6)	−0·50 (6)
C(2)	4·64 (8)	3·02 (7)	3·65 (8)	0·35 (6)	0·60 (6)	−0·42 (6)
C(3)	3·62 (7)	2·75 (7)	4·30 (8)	−0·12 (5)	1·37 (6)	−0·87 (6)
C(4)	4·92 (9)	3·88 (8)	3·06 (7)	0·19 (6)	1·20 (6)	−0·48 (6)
C(5)	4·66 (8)	3·67 (8)	3·20 (7)	0·50 (6)	1·06 (6)	0·01 (6)
C(6)	6·5 (1)	7·5 (1)	4·6 (1)	2·7 (1)	0·01 (8)	0·05 (9)
C(7)	8·2 (1)	3·65 (9)	5·8 (1)	0·03 (8)	3·0 (1)	0·40 (8)
C(8)	8·5 (1)	5·5 (1)	4·10 (9)	0·1 (1)	2·71 (9)	0·14 (8)
C(9)	4·87 (9)	4·69 (9)	5·0 (1)	0·59 (7)	−0·28 (7)	−1·78 (7)
C(10)	2·58 (6)	4·06 (8)	4·10 (8)	−0·30 (6)	0·23 (5)	−1·42 (6)
C(11)	3·06 (7)	4·65 (9)	6·2 (1)	0·21 (6)	0·89 (7)	2·49 (8)
C(12)	4·43 (8)	3·31 (7)	2·66 (6)	−0·80 (6)	−0·32 (6)	0·13 (5)
C(13)	4·37 (8)	3·60 (7)	2·70 (7)	−1·31 (6)	0·12 (6)	0·06 (5)
C(14)	2·75 (6)	3·30 (7)	2·62 (6)	−0·32 (5)	−0·02 (5)	−0·55 (5)
C(15)	3·16 (7)	3·63 (7)	2·42 (6)	−0·06 (5)	0·25 (5)	−0·02 (5)
C(16)	3·35 (7)	3·46 (7)	2·76 (6)	−0·57 (5)	0·49 (5)	−0·39 (5)
C(17)	6·9 (1)	4·21 (9)	3·99 (8)	−1·87 (8)	1·05 (8)	0·35 (7)
C(18)	3·19 (8)	6·8 (1)	4·51 (9)	−0·34 (7)	0·94 (6)	−0·70 (8)
C(19)	6·2 (1)	4·37 (9)	5·3 (1)	0·42 (8)	−1·46 (8)	0·55 (7)
C(20)	6·9 (1)	5·8 (1)	2·48 (7)	−2·18 (9)	−0·06 (7)	0·11 (7)
C(21)	2·65 (6)	2·95 (6)	2·45 (6)	0·13 (5)	0·07 (5)	−0·20 (5)
C(22)	2·58 (6)	3·95 (7)	2·64 (7)	−0·27 (5)	0·11 (5)	−0·66 (5)

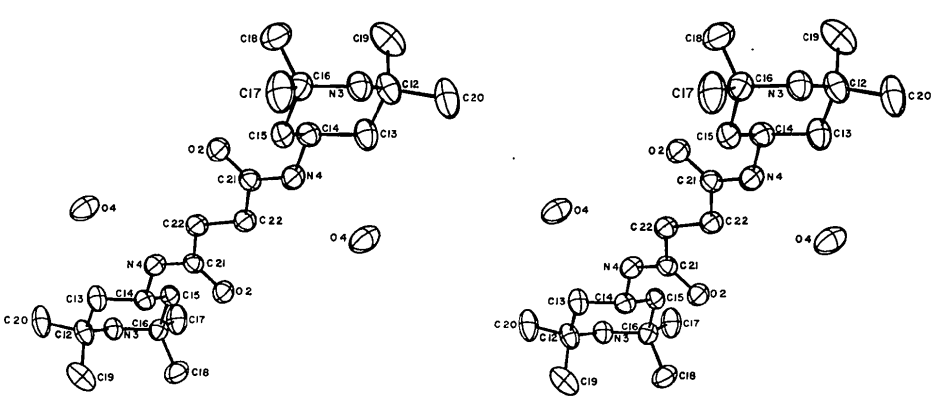

Fig. 1. Stereoscopic view of molecule II.

Table 3. *Hydrogen parameters*

Fractional coordinates are $\times 10^3$.
Temperature factor has the form $\exp(-B\sin^2\theta/\lambda^2)$.

	x	*y*	*z*	*B*
H(1)	562 (1)	265 (1)	160 (1)	4·0 (4)
H(2)	795 (1)	51 (1)	64 (1)	4·3 (4)
H(3)	705 (1)	108 (1)	181 (1)	3·6 (4)
H(4)	813 (1)	145 (1)	240 (1)	4·1 (4)
H(5)	842 (1)	247 (1)	119 (1)	3·8 (4)
H(6)	645 (1)	170 (1)	32 (1)	4·7 (4)
H(7)	716 (2)	252 (2)	−13 (2)	7·8 (6)
H(8)	−95 (3)	551 (3)	518 (2)	11·6 (9)
H(9)	−89 (2)	499 (2)	429 (2)	8·8 (7)
H(10)	489 (3)	257 (3)	43 (3)	14·2 (12)
H(11)	532 (2)	336 (2)	−39 (2)	7·6 (6)
H(12)	491 (1)	390 (1)	47 (1)	4·6 (4)
H(13)	673 (2)	485 (2)	99 (2)	8·8 (7)
H(14)	700 (2)	440 (2)	14 (1)	5·7 (5)
H(15)	770 (2)	415 (2)	105 (1)	6·3 (5)
H(16)	687 (2)	177 (2)	341 (2)	9·9 (8)
H(17)	587 (2)	160 (2)	269 (2)	7·7 (6)
H(18)	606 (2)	265 (2)	334 (2)	7·3 (6)
H(19)	820 (1)	302 (1)	320 (1)	4·4 (4)
H(20)	742 (2)	388 (2)	303 (1)	5·0 (4)
H(21)	824 (2)	359 (2)	236 (1)	6·0 (5)
H(22)	319 (2)	96 (2)	81 (2)	6·8 (6)
H(23)	275 (3)	156 (3)	144 (2)	11·8 (10)
H(24)	581 (2)	522 (2)	274 (2)	6·7 (5)
H(25)	569 (2)	437 (2)	222 (2)	6·9 (6)
H(26)	102 (1)	215 (1)	124 (1)	3·8 (4)
H(27)	428 (1)	428 (1)	304 (1)	3·6 (4)
H(28)	299 (1)	446 (1)	173 (1)	3·8 (4)
H(29)	344 (1)	340 (1)	176 (1)	3·7 (4)
H(30)	225 (1)	420 (1)	300 (1)	3·3 (3)
H(31)	251 (1)	269 (2)	372 (1)	4·6 (4)
H(32)	314 (1)	226 (1)	298 (1)	4·4 (4)
H(33)	496 (1)	563 (1)	421 (1)	4·0 (4)
H(34)	548 (1)	447 (1)	437 (1)	2·9 (3)
H(35)	148 (2)	92 (2)	321 (2)	7·2 (6)
H(36)	200 (2)	85 (2)	247 (2)	7·7 (6)
H(37)	73 (1)	91 (1)	232 (1)	4·7 (4)
H(38)	64 (2)	361 (2)	275 (1)	5·6 (5)
H(39)	51 (2)	268 (2)	350 (2)	7·2 (6)
H(40)	−4 (2)	257 (2)	250 (1)	5·6 (5)
H(41)	36 (2)	398 (2)	92 (2)	6·8 (6)
H(42)	117 (2)	484 (2)	94 (1)	5·7 (5)
H(43)	88 (2)	449 (2)	187 (2)	6·5 (5)
H(44)	218 (2)	393 (2)	6 (2)	6·9 (6)
H(45)	144 (2)	293 (2)	−0 (2)	6·7 (6)
H(46)	273 (2)	276 (2)	44 (2)	7·7 (6)

distances between the piperidyl nitrogen atoms, which are at opposite ends of the chains, are 14·45 and 14·24 Å respectively for the two molecules. The rings in both molecules are in chair conformations, and the principal difference in conformation involves the hydrogen atoms and hydrogen bonds at the terminal nitrogen atoms. In the first molecule, N(1)–H(1) is axial, and water molecule O(4) provides a hydrogen bond which is equatorial. In the second molecule, N(3)–H(26) is equatorial, and the hydrogen bond from water molecule O(3) is axial. A further difference is that H(26) appears to be involved in a very weak hydrogen bond (Table 6), while H(1) forms no hydrogen bond. We assume that these differences in bonding conformation cause the slight differences in shape of the two

Table 4. *Interatomic distances* (Å)

Molecule I		Molecule II	
O(1)—C(10)	1·221 (2)	O(2)—C(21)	1·239 (2)
N(1)—C(1)	1·479 (2)	N(3)—C(12)	1·485 (2)
N(1)—C(5)	1·489 (2)	N(3)—C(16)	1·481 (2)
N(2)—C(3)	1·460 (2)	N(4)—C(14)	1·461 (2)
N(2)—C(10)	1·331 (2)	N(4)—C(21)	1·333 (2)
C(1)—C(2)	1·539 (2)	C(12)–C(13)	1·528 (2)
C(4)—C(5)	1·536 (2)	C(15)–C(16)	1·530 (2)
C(1)—C(8)	1·525 (3)	C(12)–C(20)	1·531 (3)
C(1)—C(9)	1·521 (3)	C(12)–C(19)	1·527 (3)
C(5)—C(6)	1·539 (3)	C(16)–C(17)	1·528 (3)
C(5)—C(7)	1·512 (3)	C(16)–C(18)	1·535 (3)
C(2)—C(3)	1·524 (3)	C(13)–C(14)	1·516 (2)
C(3)—C(4)	1·509 (3)	C(14)–C(15)	1·519 (2)
C(10)–C(11)	1·508 (3)	C(21)–C(22)	1·511 (2)
C(11)–C(11)	1·493 (4)	C(22)–C(22)	1·505 (3)
Hydrogen distances			
O(3)—H(22)	0·90 (3)	O(4)—H(24)	0·81 (3)
O(3)—H(23)	0·94 (4)	O(4)—H(25)	0·80 (3)
N(1)—H(1)	0·86 (2)	N(3)—H(26)	0·98 (2)
N(2)—H(2)	0·84 (2)	N(4)—H(27)	0·86 (2)
C(2)—H(3)	0·98 (2)	C(13)–H(28)	0·88 (2)
C(2)—H(4)	1·01 (2)	C(13)–H(29)	0·96 (2)
C(3)—H(5)	1·00 (2)	C(14)–H(30)	0·98 (2)
C(4)—H(6)	1·04 (2)	C(15)–H(31)	0·97 (2)
C(4)—H(7)	1·04 (3)	C(15)–H(32)	0·97 (2)
C(6)—H(10)	1·17 (5)	C(17)–H(35)	0·85 (3)
C(6)—H(11)	0·95 (3)	C(17)–H(36)	0·98 (3)
C(6)—H(12)	0·97 (3)	C(17)–H(39)	1·02 (3)
C(7)—H(13)	0·97 (3)	C(18)–H(38)	1·03 (3)
C(7)—H(14)	0·97 (3)	C(18)–H(39)	1·05 (3)
C(7)—H(15)	0·98 (3)	C(18)–H(40)	0·98 (3)
C(8)—H(16)	0·88 (4)	C(19)–H(41)	0·97 (3)
C(8)—H(17)	1·00 (3)	C(19)–H(42)	0·95 (3)
C(8)—H(18)	1·04 (3)	C(19)–H(43)	1·06 (3)
C(9)—H(19)	0·90 (3)	C(20)–H(44)	1·05 (3)
C(9)—H(20)	0·97 (3)	C(20)–H(45)	0·98 (3)
C(9)—H(21)	1·01 (3)	C(20)–H(46)	1·05 (3)
C(11)–H(8)	1·01 (4)	C(22)–H(33)	1·05 (2)
C(11)–H(9)	1·02 (4)	C(22)–H(34)	0·96 (2)

Table 5. *Selected bond angles* (°)

Molecule I		Molecule II	
C(11)–C(11)–C(10)	113·0 (2)	C(22)–C(22)–C(21)	113·1 (2)
C(11)–C(10)–O(1)	122·2 (2)	C(22)–C(21)–O(2)	122·5 (2)
C(11)–C(10)–N(2)	115·7 (2)	C(22)–C(21)–N(4)	115·0 (2)
O(1)—C(10)–N(2)	122·1 (2)	O(2)—C(21)–N(4)	122·4 (2)
C(10)–N(2)—C(3)	124·5 (2)	C(21)–N(4)—C(14)	122·8 (2)
N(2)—C(3)—C(2)	110·0 (2)	N(4)—C(14)–C(13)	108·8 (2)
C(3)—C(2)—C(1)	113·6 (2)	C(14)–C(13)–C(12)	113·0 (2)
C(2)—C(1)—N(1)	112·2 (2)	C(13)–C(12)–N(3)	107·2 (2)
C(2)—C(1)—C(9)	110·8 (2)	C(13)–C(12)–C(19)	111·8 (2)
C(2)—C(1)—C(8)	108·4 (2)	C(13)–C(12)–C(20)	109·6 (2)
C(8)—C(1)—C(9)	108·5 (2)	C(19)–C(12)–C(20)	108·0 (2)
C(8)—C(1)—N(1)	105·7 (2)	C(20)–C(12)–N(3)	105·2 (2)
C(9)—C(1)—N(1)	111·0 (2)	C(19)–C(12)–N(3)	114·8 (2)
C(1)—N(1)—C(5)	119·9 (2)	C(12)–N(3)—C(16)	119·8 (2)
C(4)—C(5)—N(1)	111·1 (2)	C(15)–C(16)–N(3)	107·1 (2)
C(4)—C(5)—C(6)	109·3 (2)	C(15)–C(16)–C(17)	110·4 (2)
C(4)—C(5)—C(7)	110·7 (2)	C(15)–C(16)–C(18)	111·2 (2)
C(6)—C(5)—C(7)	109·2 (2)	C(17)–C(16)–C(18)	107·0 (2)
C(6)—C(5)—N(1)	105·5 (2)	C(17)–C(16)–N(3)	105·8 (2)
C(7)—C(5)—N(1)	110·9 (2)	C(18)–C(16)–N(3)	115·4 (2)
C(5)—C(4)—C(3)	114·1 (2)	C(16)–C(15)–C(14)	111·7 (2)
C(4)—C(3)—C(2)	109·4 (2)	C(15)–C(14)–C(13)	109·7 (2)
C(4)—C(3)—N(2)	110·3 (2)	C(15)–C(14)–N(4)	112·1 (2)

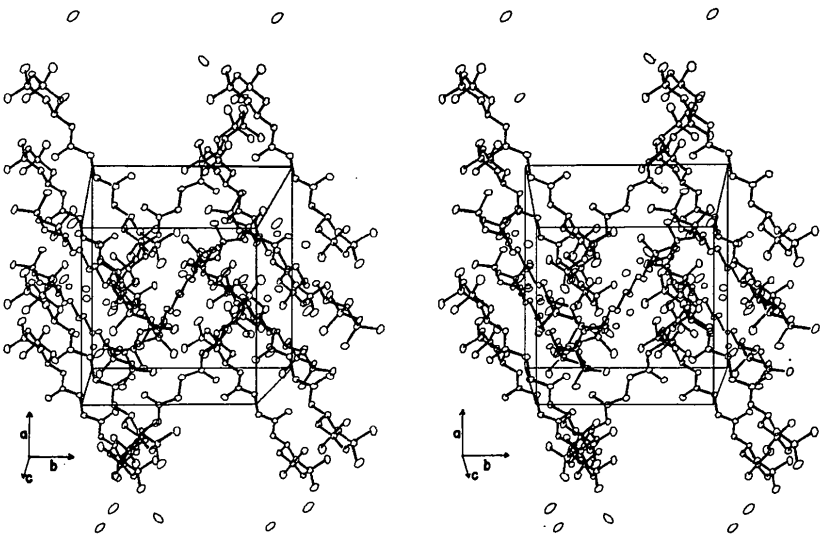

Fig. 2. Stereoscopic view of a unit cell showing the packing.

molecules. The shapes of the two rings can be made identical if various atoms are shifted 0·1 Å or less.

Table 6. *Hydrogen-bond distances* (Å)

O(3)–H(22)···O(2)	2·863 (2)
O(3)–H(23)···N(3)	2·890 (2)
O(4)–H(24)···O(3)	2·813 (3)
O(4)–H(25)···N(1)	2·905 (2)
N(2)–H(2)····O(2)	2·953 (2)
N(3)–H(26)···O(1)	3·069 (3)
N(4)–H(27)···O(4)	2·856 (2)

Chemically equivalent bond lengths in the two molecules differ by two or three times as much as would be expected from the estimated standard deviations. Because a full-matrix procedure could not be used, the estimated standard deviations may be too low. Thermal motion, for which no correction was practicable, may also contribute to these differences. Thus the corresponding bond lengths in the two molecules may be regarded as identical.

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