Crystal Structure of a Very Hindered Olefin: 1,1-Diphenyl-2,2-di-t-butylethylene † at —155 °C

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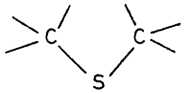
An *X*-ray crystal structure determination at −155 °C of 1,1-diphenyl-2,2-di-t-butylethylene, $C_{22}H_{28}$ [monoclinic, space group *C*2/*c*, *a* = 32.703(3), *b* = 6.085(1), *c* = 20.747(2) Å, β = 122.40(1)°, *Z* = 8, final *R*0. 049 for 3 777 independent reflections) shows the steric hindrance effect on bond distances, valence angles, and twist of the central double bond (24°). Mean single-bond distances are: $C(sp^2)-C(sp^2)$ 1.504, $C(sp^2)-C(sp^3)$ 1.574, and $C(sp^3)-C(sp^3)$ 1.546 Å. Valence angles tend to narrow the hindrance of the t-butyl groups. The shortest 1,5-intramolecular contacts are C(Ph) ••• $C(Bu^t)$ 2.80 and $C(Bu^t)$ ••• $C(Bu^t)$ 3.13 Å. Intermolecular contacts are as expected. The conformation of the isolated molecule should differ little from that found in the crystal.

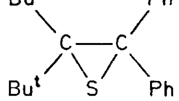
THE synthesis of some overcrowded olefins has been accomplished recently *via* the addition of a diazo-compound to a thione, giving rise to a Δ^3-1,3,4-thiadiazoline (I), and by subsequent extrusion of nitrogen and sulphur.[1] In the synthesis of 1,1-diphenyl-2,2-di-t-butylethylene the first step of the extrusion process led to 2,2-diphenyl-3,3-di-t-butylthiiran (II) for which the crystal structure of two stable phases has been recently studied.[2]

An even more interesting structure is that of the final product itself, the olefin (III), for which strong steric hindrance is expected to deform the central $C(sp^2)=C(sp^2)$ system.

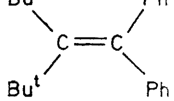
The crystal structure of (III) was determined by direct methods (MULTAN).[3] Atom co-ordinates and thermal



(I)



(II)



(III)

parameters are listed in Tables 1 and 2, bond lengths and angles in Tables 3 and 4. A view of the molecular

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† Systematic name 3,3-dimethyl-1,1-diphenyl-2-t-butylbut-1 ene.

[1] D. H. R. Barton, F. S. Guziec, jun., and I. Shahak, *J.C.S. Perkin I*, 1974, 1794.

[2] A. Mugnoli and M. Simonetta, *Acta Cryst.*, 1976, **B32**, 1962.

[3] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

TABLE 1

Carbon atom parameters ($\times 10^4$), with standard deviations in parentheses *

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	3 612(0)	6 682(2)	9 606(1)	4(0)	67(3)	10(0)	−1(1)	3(0)	−1(1)
C(2)	3 850(0)	7 196(2)	9 172(1)	3(0)	113(3)	8(0)	3(1)	2(0)	5(1)
C(3)	3 800(0)	5 833(2)	8 592(1)	4(0)	146(3)	10(0)	2(1)	3(0)	−4(1)
C(4)	3 990(0)	6 455(2)	8 161(1)	5(0)	243(4)	10(0)	11(1)	4(0)	1(1)
C(5)	4 225(0)	8 459(2)	8 291(1)	5(0)	244(4)	16(0)	14(1)	7(0)	30(1)
C(6)	4 269(0)	9 844(2)	8 855(1)	6(0)	153(4)	22(0)	5(1)	8(0)	22(1)
C(7)	4 079(0)	9 217(2)	9 287(1)	5(0)	122(3)	14(0)	2(1)	5(0)	5(1)
C(8)	3 076(0)	6 480(2)	9 038(1)	4(0)	114(3)	8(0)	−1(1)	4(0)	−5(1)
C(9)	2 840(0)	4 495(2)	8 956(1)	6(0)	120(3)	11(0)	−4(1)	5(0)	−7(1)
C(10)	2 351(0)	4 239(2)	8 391(1)	6(0)	188(4)	16(0)	−16(1)	7(0)	−23(1)
C(11)	2 096(0)	5 952(3)	7 898(1)	4(0)	279(4)	11(0)	−5(1)	3(0)	−20(1)
C(12)	2 329(0)	7 911(2)	7 960(1)	5(0)	221(4)	11(0)	9(1)	4(0)	3(1)
C(13)	2 816(0)	8 167(2)	8 521(1)	5(0)	130(3)	11(0)	1(1)	4(0)	2(1)
C(14)	3 842(0)	6 514(2)	10 378(1)	4(0)	68(3)	10(0)	−2(1)	3(0)	−1(1)
C(15)	4 392(0)	5 857(2)	10 877(1)	4(0)	112(3)	9(0)	1(1)	3(0)	2(1)
C(16)	4 590(0)	4 861(2)	10 413(1)	5(0)	145(3)	13(0)	9(1)	4(0)	3(1)
C(17)	4 739(0)	7 761(2)	11 336(1)	4(0)	178(4)	12(0)	−6(1)	3(0)	−9(1)
C(18)	4 454(0)	3 966(2)	11 421(1)	7(0)	155(4)	15(0)	9(1)	5(0)	18(1)
C(19)	3 555(0)	6 937(2)	10 780(1)	5(0)	100(3)	10(0)	−1(1)	4(0)	0(1)
C(20)	3 871(0)	8 072(2)	11 565(1)	7(0)	142(3)	12(0)	−4(1)	5(0)	−8(1)
C(21)	3 332(0)	4 850(2)	10 894(1)	7(0)	130(3)	15(0)	−7(1)	7(0)	−1(1)
C(22)	3 136(0)	8 594(2)	10 327(1)	6(0)	147(3)	13(0)	6(1)	6(0)	0(1)

* Thermal factors are of the form: $\exp[-(B_{11}h^2 + 2B_{12}hk + \ldots)]$.

TABLE 2

Parameters for the hydrogen atoms (positional parameters $\times 10^3$)

	x	y	z	B/Å^2
H(1)	364	445	851	2.2
H(2)	395	546	776	3.8
H(3)	436	888	799	3.6
H(4)	443	1 128	894	3.4
H(5)	411	1 026	969	2.7
H(6)	302	330	929	2.8
H(7)	219	281	836	3.2
H(8)	176	577	750	3.5
H(9)	216	911	761	3.6
H(10)	298	960	856	2.2
H(11)	436	373	1 004	2.6
H(12)	490	412	1 078	2.7
H(13)	467	599	1 014	2.5
H(14)	508	720	1 158	3.2
H(15)	470	901	1 098	3.4
H(16)	470	837	1 173	3.4
H(17)	481	354	1 173	3.4
H(18)	425	264	1 112	3.4
H(19)	435	434	1 179	3.2
H(20)	417	719	1 196	3.0
H(21)	398	954	1 152	2.7
H(22)	367	831	1 178	2.6
H(23)	310	415	1 041	2.9
H(24)	358	370	1 122	3.6
H(25)	316	529	1 115	3.3
H(26)	286	793	986	3.2
H(27)	326	991	1 018	2.9
H(28)	302	908	1 066	2.7

TABLE 3

Bond lengths (Å)

C(1)–C(2)	1.503	C(12)–C(13)	1.389
C(2)–C(3)	1.397	C(8)–C(13)	1.397
C(3)–C(4)	1.390	C(1)–C(14)	1.360
C(4)–C(5)	1.389	C(14)–C(15)	1.572
C(5)–C(6)	1.385	C(15)–C(16)	1.545
C(6)–C(7)	1.391	C(15)–C(17)	1.544
C(2)–C(7)	1.393	C(15)–C(18)	1.547
C(1)–C(8)	1.505	C(14)–C(19)	1.575
C(8)–C(9)	1.394	C(19)–C(20)	1.548
C(9)–C(10)	1.397	C(19)–C(21)	1.544
C(10)–C(11)	1.384	C(19)–C(22)	1.547
C(11)–C(12)	1.383		

structure in the crystal together with the numbering of atoms is given on the thermal ellipsoids plot [4] of Figure 1. H–C(Ph) and H–C(Me) bond distances are in the ranges 0.95—1.01 and 0.97—1.02 Å. Phenyl C–C–H, t-butyl C–C–H, and H–C–H bond angles are in the ranges 118—122, 107—115, and 106—110°.

TABLE 4

Bond angles (°)

C(2)–C(1)–C(8)	107.9	C(11)–C(12)–C(13)	120.2
C(2)–C(1)–C(14)	125.8	C(8)–C(13)–C(12)	120.9
C(8)–C(1)–C(14)	126.3	C(1)–C(14)–C(15)	120.6
C(1)–C(2)–C(3)	122.1	C(1)–C(14)–C(19)	120.1
C(1)–C(2)–C(7)	119.1	C(15)–C(14)–C(19)	119.2
C(3)–C(2)–C(7)	118.4	C(14)–C(15)–C(16)	113.8
C(2)–C(3)–C(4)	120.5	C(14)–C(15)–C(17)	114.9
C(3)–C(4)–C(5)	120.4	C(14)–C(15)–C(18)	109.1
C(4)–C(5)–C(6)	119.7	C(16)–C(15)–C(17)	105.2
C(5)–C(6)–C(7)	119.8	C(16)–C(15)–C(18)	103.1
C(2)–C(7)–C(6)	121.2	C(17)–C(15)–C(18)	110.1
C(1)–C(8)–C(9)	120.2	C(14)–C(19)–C(20)	112.3
C(1)–C(8)–C(13)	121.1	C(14)–C(19)–C(21)	114.3
C(9)–C(8)–C(13)	118.3	C(14)–C(19)–C(22)	111.7
C(8)–C(9)–C(10)	120.6	C(20)–C(19)–C(21)	108.0
C(9)–C(10)–C(11)	120.2	C(20)–C(19)–C(22)	102.9
C(10)–C(11)–C(12)	119.7	C(21)–C(19)–C(22)	107.0

The estimated standard deviations of the co-ordinates, as derived from the residuals and the diagonal elements of the least-squares inverse matrix, correspond to standard deviations of the order of 0.002 Å and 0.1° in bond lengths and angles involving only carbon atoms, and of 0.02 Å, 1°, and 1.3° in C–H bond distances and C–C–H and H–C–H bond angles, respectively. A more realistic estimate of the accuracy of the results is probably obtained by multiplying these calculated standard deviations by a factor of two.[5]

The molecular overcrowding reflects on the central

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[4] C. K. Johnson, ORTEP, U.S. Atomic Energy Commission Report ORNL 3794, 1965.

[5] W. C. Hamilton and S. C. Abrahams, *Acta Cryst.*, 1970, **A26**, 18.

double-bond distance (1.360 Å), which is significantly longer than commonly accepted values [1.337 ± 0.006 (ref. 6), 1.335 ± 0.010 Å (ref. 7)]. Even more obviously, steric hindrance causes the central $C(sp^2)=C(sp^2)$ system to deviate from planarity. The dihedral angle between the least-squares planes[8] through atoms C(1), C(2), C(8), and C(14), and C(1), C(14), C(15), and C(19) corresponds to a twist of the double bond by 24°. In spite of this, there are some short intramolecular distances (see Table 5), especially between C(Ph) and $C(Bu^t)$ atoms. There are no short C(Ph) ··· C(Ph) intramolecular contacts; with reference to the C(1), C(2), C(8), C(14) plane, the groups C(1), C(2)—(7), and C(1), C(8)—(13), are rotated by 61 and 59°, respectively.† In fact, the strain due to the phenyl groups can be relieved by rotation; in tetraphenylethylene[9] the torsion angles of phenyl rings are in the range 42.9 to 57.1° and the twist angle around the central bond (1.356 Å) is just 8.4°.

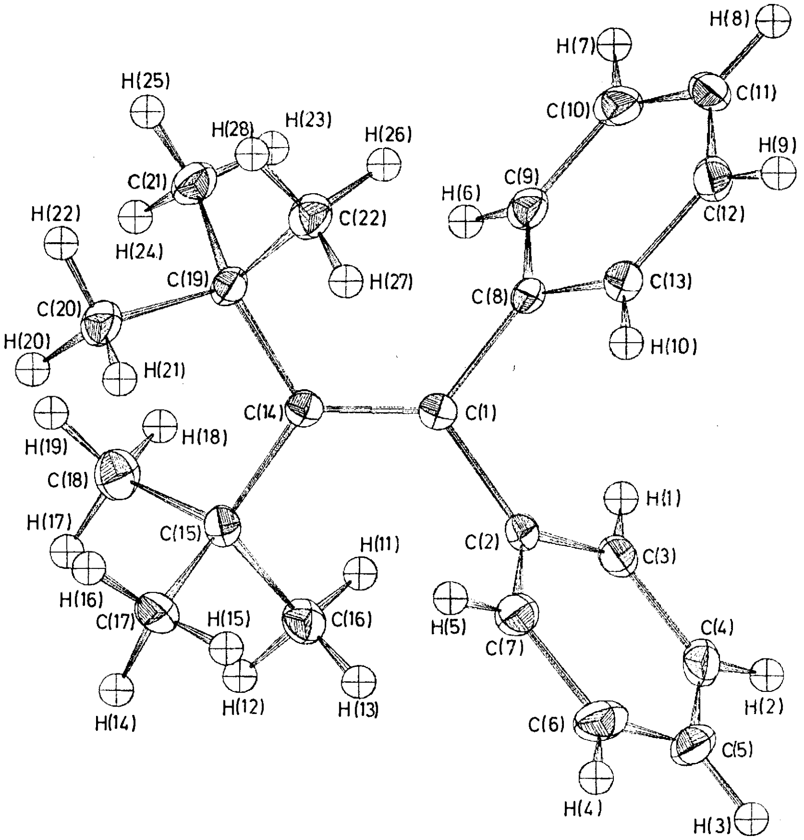

FIGURE 1 Numbering of atoms and temperature ellipsoids of one molecule of $C_{22}H_{28}$ viewed along the normal to the C(1), C(2), C(8), C(14) plane. Carbon atoms are drawn at 0.50 probability; hydrogen atoms, treated as isotropic, are on an arbitrary scale

TABLE 5

Some 1,5- and 1,6-intramolecular contacts (Å)

C(3) ··· C(13)	3.45	C(9) ··· C(21)	3.44
C(2) ··· C(16)	2.80	C(9) ··· C(22)	3.51
C(3) ··· C(16)	3.29	C(13) ··· C(22)	3.32
C(7) ··· C(15)	3.53	C(17) ··· C(20)	3.13
C(7) ··· C(16)	3.33	C(18) ··· C(20)	3.25
C(8) ··· C(22)	2.88	C(18) ··· C(21)	3.26
C(9) ··· C(19)	3.54		

According to the steric hindrance, all C–C bond distances (except those in the phenyl rings) show some lengthening. Mean single-bond distances are: $C(sp^2)$–$C(sp^2)$ 1.504, $C(sp^2)$–$C(sp^3)$ 1.574, and $C(sp^3)$–$C(sp^3)$ 1.546 Å, compared with the corresponding suggested values[7] of 1.47—1.48, 1.501, and 1.526 Å.

A typical trend in bond-length and bond-angle values can be observed in comparing structural results for a sequence of molecules affected by increasing steric hindrance due to the presence of one, two, or three t-butyl groups bonded to a single (C or H) atom, as in isobutane,[10,11] 1,1-diphenyl-2,2-di-t-butylethylene, and tri-t-butylmethane;[12] for the first and last compounds

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† The two phenyl rings, C(2)—(7) and C(8)—(13) are planar within 0.012 and 0.016 Å respectively, but the repulsion from the t-butyl groups causes the C(1), C(2), C(5) and C(1), C(8), C(11) axes to be bent at 174.6 and 175.3°, respectively.

[6] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1968.

[7] D. R. Lide, jun., *Tetrahedron*, 1962, **17**, 125.

[8] V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, 1959, **12**, 600.

[9] A. Hoekstra and A. Vos, *Acta Cryst.*, 1975, **B31**, 1722.

[10] D. R. Lide, jun., *J. Chem. Phys.*, 1960, **33**, 1519.

[11] R. L. Hilderbrandt and J. D. Wieser, *J. Mol. Structure*, 1973, **15**, 27.

[12] H. B. Bürgi and L. S. Bartell, *J. Amer. Chem. Soc.*, 1972, **94**, 5236; L. S. Bartell and H. B. Bürgi, *ibid.*, **94**, 5239.

the geometry has been determined in the gas phase by use of various methods, such as microwave and i.r. spectroscopy, electron diffraction, and molecular mechanics. Besides an apparent shortening of the C–H bond lengths obtained by *X*-ray diffraction for the present compound, and even being aware of the different meaning of structural parameters found with different techniques, the general trend which emerges from Table 6 is towards an increase of peripheral bond lengths and a narrowing of branched (aliphatic) groups.

TABLE 6

Mean structural parameters for isobutane, 1,1-diphenyl-2,2-di-t-butylethylene, and tri-t-butylmethane; distances (Å) and angles (°). Subscripts: m = methyl, te = tertiary, tr = trigonal, q = quaternary

	C_4H_{10} [a]	C_4H_{10} [b]	$C_{22}H_{28}$	$C_{13}H_{28}$ [c]
$C-H_m$	1.09—1.10	1.113	1.00	1.111
C–C			1.574 [d]	1.611 [e]
C–C	1.525	1.535 [f]	1.546 [g]	1.548 [g]
C–C–C			119.2 [h]	116.0 [i]
C–C–C			113 [j]	113.0 [k]
C–C–C	111.15 [l]	110.8 [l]	106 [m]	105.8 [m]
$C_q-C_m-H_m$			111	114.2

[a] Ref. 10. [b] Ref. 11. [c] Ref. 12. [d] $C_{tr}-C_q$. [e] $C_{te}-C_q$. $C_{te}-C_m$. [g] C_q-C_m. [h] $C_q-C_{tr}-C_q$. [i] $C_q-C_{te}-C_q$. [j] $C_{tr}-C_q-C_m$. [k] $C_{te}-C_q-C_m$. [l] $C_m-C_{te}-C_m$. [m] $C_m-C_q-C_m$.

On the other hand, intermolecular contacts are in the normal range. A plotter output[4] of the packing of molecules in the crystal is shown in Figure 2. There are only three contacts shorter by 0.1 Å or more with respect to the sum of van der Waals radii:[13] C(16) · · · C(16) (at $1-x$, $1-y$, $2-z$) 3.88, C(22) · · · C(22) (at $\frac{1}{2}-x$, $\frac{3}{2}-y$, $2-z$) 3.86, and H(5) · · · H(11) (at x, $1+y$, z) 2.24 Å. We may therefore confidently assume that the conformation of the isolated molecule is not far from that found in the crystal phase.

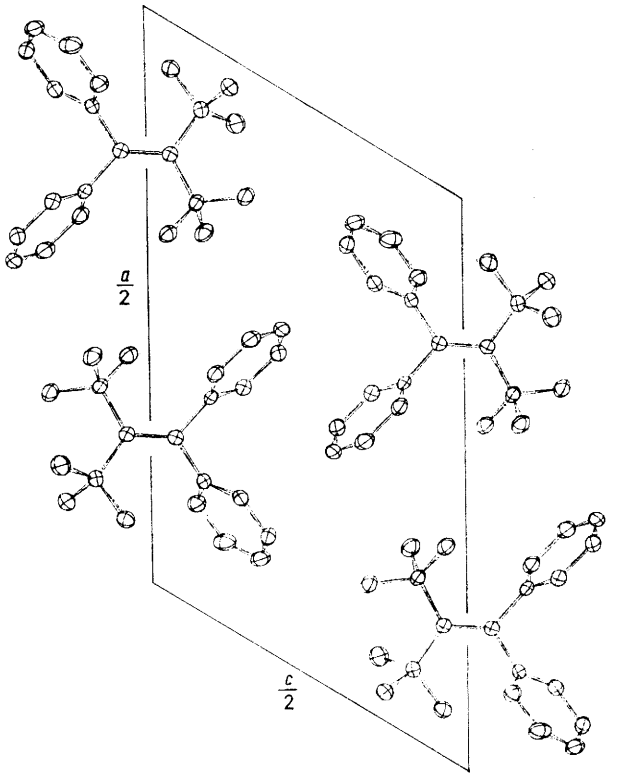

FIGURE 2 Packing of molecules in the crystal, as seen along the *y* axis

EXPERIMENTAL

1,1-Diphenyl-2,2-di-t-butylethylene crystallizes as transparent parallelepipeds. A single crystal was cut and rounded by partial solution in ethanol to a nearly spherical shape (diameter *ca.* 0.3 mm). Lattice parameters and intensities were obtained by use of a Syntex P$\bar{1}$ four-circle diffractometer equipped with graphite monochromator and LT 1 low-temperature device, with the outlet nozzle of the cold nitrogen stream fixed to the χ arc along the ϕ axis in front of the goniometer head. The nitrogen was allowed to flow at constant rate in order to maintain the temperature of the crystal at −155 °C. Lattice parameters were obtained from a least-squares fit of 21 reflections (plus some of their equivalents).

Crystal Data.—$C_{22}H_{28}$, m.p. 141 °C. Monoclinic, $T = -155$ °C, $a = 32.703(3)$, $b = 6.085(1)$, $c = 20.747(2)$ Å, $\beta = 122.40(1)°$, $U = 3\,486$ Å^3, $Z = 8$, $D_c = 1.114$, $D_m = 1.066$ g cm^{-3} at room temperature (by flotation), $F(000) = 1\,280$. Mo-K_α *X*-radiation, $\lambda = 0.710\,7$ Å; μ (Mo-K_α) = 0.7 cm^{-1}. Space group *Cc* or *C2/c* from systematic absences; evidence for *C2/c* given by statistics of normalized structure factors.

Collection of Intensities and Structure Determination.—Diffracted intensities were measured out to 2θ 55° by the ω-scan technique, with scan range 0.8° and variable scan

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[13] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.

speed. The right and left backgrounds were counted for half the total scanning time 0.8° apart from the peak. Two standard reflections monitored after each group of 50 reflections showed no significant change during data collection. In the explored range, 3 991 independent reflections were measured, of which 3 777 had intensity above background. Intensities and their standard deviations were corrected for Lorentz and polarization but not for absorption effects.

The structure was solved by direct methods.[3] The solution corresponding to the best figure-of-merit led to an E map from whose peaks the co-ordinates of all the carbon atoms were derived.

Structure Refinement.—Refinement was accomplished on all the 3 777 observed reflections by a full-matrix least-squares process using a modified version of the program ORFLS.[14] The function minimized was $\Sigma w(\Delta F)^2$, with weights $w = 1/\sigma^2(F)$. Atomic scattering factors for carbon were taken from ref. 15 and for hydrogen from ref. 16. After four cycles of isotropic refinement, a difference map showed all hydrogen atom positions. In the following cycles, carbon atoms (treated as anisotropic) and an extinction correction parameter g [17] were allowed to refine.

All hydrogen atoms were then refined isotropically; because of computer-core size limitation, hydrogen and carbon atoms were refined in four subsequent separate cycles. At this point the refinement was considered complete, the highest shift being $<0.25\sigma$, and most shifts being $<0.1\sigma$. The final R was 0.049 for all 3 777 observed reflections, and 0.054 over all 3 991 data. A final difference-Fourier synthesis, calculated with all observed reflections, showed no significant features. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 21808 (21 pp., 1 microfiche).* The final value for the extinction parameter g was 7.4×10^{-7}.

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[6/272 *Received, 9th February,* 1976]

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* See Notice to Authors No. 7 in *J.C.S. Perkin II*, 1975, Index issue.

[14] W. R. Busing, K. O. Martin, and H. A. Levy, ORFLS, U.S. Atomic Energy Commission Report ORNL TM 305, 1962.

[15] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[16] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[17] W. H. Zachariasen, *Acta Cryst.*, 1963, **16**, 1139; A. C. Larson, *ibid.*, 1967, **23**, 664; K. A. Kerr and J. P. Ashmore, *ibid.*, 1974, **A30**, 176.