The packing of the molecules in the unit cell is shown in Fig. 2. Intermolecular contacts less than 3·2 Å are given in Table 2.

The authors would like to thank Dr M. Ahmad for kindly supplying the crystals.

References

Balasubramanian, S. K., Barton, D. H. R. & Jackman, L. M. (1962). *J. Chem. Soc.* pp. 4816–4820.

Barton, D. H. R. & Elad, D. (1956). *J. Chem. Soc.* pp. 2085–2090; 2090–2095.

Barton, D. H. R., Overton, K. H. & Wylie, A. (1962). *J. Chem. Soc.* pp. 4809–4815.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, USA.

Cheung, K. K., Melville, D., Overton, K. H., Robertson, J. M. & Sim, G. A. (1966). *J. Chem. Soc. B*, pp. 853–861.

Coppens, P., Leiserowitz, L. & Rabinovich, D. (1965). *Acta Cryst.* **18**, 1035–1038.

Davis, R. E. & Harris, D. R. (1970). *DAESD*. Roswell Park Mem. Inst., USA.

Ferguson, G. & Islam, K. M. S. (1969). *J. Chem. Soc. B*, pp. 162–170.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)

Jacobson, R. A. & Lawton, S. L. (1965). *TRACER*. United States Energy Commission, Report TID-4500. Iowa State Univ., USA.

Johnson, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Khuda, M. Q., Khaleque, A. & Roy, N. (1964). *Scientific Res. (Dacca, Bangladesh)*, **1**, 177.

Overton, K. H., Weir, N. G. & Wylie, A. (1961). *Proc. Chem. Soc.* pp. 211–212.

Overton, K. H., Weir, N. G. & Wylie, A. (1966). *J. Chem. Soc. C*, pp. 1482–1490.

Roberts, P. & Sheldrick, G. M. (1976). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.

Sheldrick, G. M. (1974). *SHELX*. Program for crystal structure determination. Univ. of Cambridge, England.

Acta Cryst. (1986). C**42**, 1220–1222

Structure of (*Z*)-1,2-Diphenyl-2-*p*-tolylvinyl 2,2,2-Trifluoroethyl Ether

By Yaoguang Luo, Richard J. Barton and Beverly E. Robertson

Faculty of Science, University of Regina, Regina, Saskatchewan, Canada S4S 0A2

and Choi Chuck Lee and Dave Wanigasekera

Department of Chemistry, University of Saskatchewan, Saskatoon, Saskatchewan, Canada S7N 0W0

(*Received* 15 *January* 1986; *accepted* 24 *March* 1986)

Abstract. $C_{23}H_{19}F_3O$, $M_r = 368{\cdot}40$, monoclinic, $P2_1$, $a = 10{\cdot}590\,(2)$, $b = 9{\cdot}634\,(2)$, $c = 9{\cdot}582\,(2)$ Å, $\beta = 95{\cdot}57\,(2)°$, $V = 972{\cdot}98$ Å^3, $Z = 2$, $D_x = 1{\cdot}26$ g cm^{-3}, $D_m = 1{\cdot}23$ g cm^{-3} by flotation, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo}) = 0{\cdot}90$ cm^{-1}, $F(000) = 384$, $T = 291$ K, $R = 0{\cdot}061$ for 1745 observed reflections. The configuration of the molecule is the (*Z*) isomer. The bond lengths and angles are in agreement with those of similar compounds. The molecule has a propeller conformation.

Introduction. In order to study the solvolytic rearrangement of ^{13}C or ^{14}C labeled (*E*)- and (*Z*)-1,2-diphenyl-2-tolylvinyl bromide, the structure of the title compound has been determined to verify the configuration assignment based on ^{1}H NMR spectra.

Experimental. Crystals of the title compound obtained from the reaction of 1,2-diphenyl-2-tolylvinyl bromide in trifluoroethanol and 2,6-lutidine, and recrystallized from 90% ethanol (Lee & Wanigasekera, 1986). A pale yellow crystal of dimensions 0·1 × 0·3 × 0·3 mm chosen for study. Intensity data collected with a modified Picker four-circle diffractometer, $\theta/2\theta$ scan technique, graphite-monochromated Mo $K\alpha$ radiation. Three standard reflections monitored after every 47 reflections. The intensity of the standard reflections did not change significantly. Two equivalent sets of data collected in the 2θ range 3 to 53° at 291 ± 2 K in octants $(+h,+k,+l)$ and $(-h,-k,-l)$ with $0 \le h \le 13$, $0 \le k \le 12$ and $0 \le l \le 12$. After averaging, 2128 independent reflections used in the structure determination, of which 1745 reflections were considered as observed with $I > 2\sigma(I)$. Lorentz and polarization corrections. Absorption corrections not applied. The *E* map obtained from direct methods using the *XTAL* system of crystallographic programs (Stewart & Hall, 1984) gave 23 of 27 non-hydrogen atoms. A subsequent difference Fourier synthesis gave all non-hydrogen atoms. After several cycles of full-matrix least-squares anisotropic refinement with all non-hydrogen atoms, difference Fourier syntheses gave only six of the 19 H atoms; remaining H atoms were placed at idealized positions with C—H = 1·00 Å. Tem-

0108-2701/86/091220-03$01.50

perature factors of the methyl and methylene H atoms were set at the equivalent isotropic value of the C atoms to which they were bonded and their temperature factors and positional parameters were constrained during subsequent refinement. Other H atoms refined isotropically. R decreased to $R = 0{\cdot}061$ and $wR = 0{\cdot}048$ with $w = 1/\sigma^2(F)$ in the final cycle of refinement. $S = 0{\cdot}71$, $(\Delta/\sigma)_{\max} = 0{\cdot}095$. Highest peak in final difference Fourier map 0·35 e Å^{-3}. The molecule does not contain any elements with significant anomalous scattering. Therefore, no attempt was made to determine the chirality of the crystal. Atomic scattering factors from Cromer & Mann (1968). All computations were carried out with a VAX11/750 computer and the *XTAL* system of crystallographic programs.

Discussion. Table 1 lists final fractional atomic coordinates and isotropic thermal parameters.[*] Bond lengths and angles are listed in Table 2. A stereoview of the molecule is given in Fig. 1.

The result confirms the previous configuration assignment based on the ^{1}H NMR spectra. All aryl rings are planar within experimental error. They are twisted with respect to each other at angles of 86·5 (3), 55·2 (2) and 81·3 (2)° to form a propeller conformation. The twist of the vinylic C=C double bond, defined by the torsional angle C(5)—C(1)—C(2)—C(11), is 5·7 (7)°. The presence of the propeller conformation and twisted vinylic double bond in the triarylvinyl-*X* system is due mainly to the steric interaction among neighbouring aryl groups (Kaftory, Apeloig & Rappoport, 1985). The C(1)—C(2) bond length of 1·328 (6) Å is similar to that in other triarylvinyl systems (Kaftory, Biali & Rappoport, 1985) and is also

Table 1. *Fractional atomic coordinates* (×10^4) *with e.s.d.'s in parentheses and thermal parameters* (Å^2 × 10^2)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
F(1)	7114 (3)	1903 (6)	7221 (3)	9·1
F(2)	6057 (4)	3375 (8)	5898 (6)	14·8
F(3)	5613 (4)	3013 (7)	7961 (5)	14·6
O(1)	3899 (3)	1954 (6)	5889 (3)	4·6
C(1)	2841 (4)	1062	5617 (5)	3·9
C(2)	2183 (4)	1181 (6)	4371 (4)	3·7
C(3)	5055 (4)	1315 (7)	6353 (5)	5·3
C(4)	5946 (5)	2393 (9)	6827 (6)	6·9
C(5)	2531 (4)	233 (7)	6845 (4)	4·0
C(6)	2651 (5)	801 (8)	8181 (5)	5·7
C(7)	2359 (6)	42 (8)	9332 (6)	6·6
C(8)	1979 (6)	−1329 (8)	9180 (6)	6·6
C(9)	1852 (5)	−1930 (8)	7863 (6)	5·4
C(10)	2142 (4)	−1144 (7)	6703 (5)	4·7
C(11)	897 (4)	532 (7)	4091 (4)	4·3
C(12)	−69 (5)	750 (7)	4969 (5)	5·2
C(13)	−1228 (5)	138 (8)	4680 (6)	5·7
C(14)	−1486 (6)	−714 (8)	3525 (6)	6·3
C(15)	−556 (6)	−931 (8)	2648 (6)	6·4
C(16)	617 (5)	−300 (8)	2931 (5)	5·1
C(17)	2597 (4)	2076 (7)	3219 (4)	4·1
C(18)	1752 (5)	2948 (8)	2459 (5)	5·1
C(19)	2104 (5)	3787 (8)	1407 (5)	5·3
C(20)	3329 (5)	3775 (8)	1033 (5)	5·0
C(21)	4189 (5)	2865 (8)	1729 (5)	5·5
C(22)	3826 (5)	2008 (8)	2808 (5)	5·0
C(23)	3724 (5)	4719 (8)	−119 (5)	7·2

Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

C(1)—C(2)	1·328 (6)	C(2)—C(11)	1·499 (5)
C(1)—O(1)	1·416 (5)	C(11)—C(12)	1·402 (7)
O(1)—C(3)	1·403 (5)	C(12)—C(13)	1·366 (8)
C(3)—C(4)	1·447 (9)	C(13)—C(14)	1·384 (9)
C(4)—F(1)	1·343 (7)	C(14)—C(15)	1·371 (9)
C(4)—F(2)	1·312 (10)	C(15)—C(16)	1·386 (8)
C(4)—F(3)	1·318 (9)	C(16)—C(11)	1·379 (8)
C(1)—C(5)	1·485 (7)	C(2)—C(17)	1·499 (7)
C(5)—C(6)	1·387 (7)	C(17)—C(18)	1·382 (8)
C(6)—C(7)	1·383 (9)	C(18)—C(19)	1·372 (9)
C(7)—C(8)	1·384 (11)	C(19)—C(20)	1·379 (7)
C(8)—C(9)	1·383 (8)	C(20)—C(21)	1·387 (8)
C(9)—C(10)	1·403 (8)	C(21)—C(22)	1·406 (7)
C(10)—C(5)	1·392 (10)	C(22)—C(17)	1·397 (8)
C(20)—C(23)	1·520 (8)		

C(2)—C(1)—O(1)	116·7 (8)	C(1)—O(1)—C(3)	116·3 (5)
O(1)—C(3)—C(4)	107·9 (6)	C(3)—C(4)—F(1)	113·0 (6)
C(3)—C(4)—F(2)	113·8 (5)	C(3)—C(4)—F(3)	111·5 (5)
F(1)—C(4)—F(2)	107·7 (5)	F(1)—C(4)—F(3)	103·9 (5)
F(2)—C(4)—F(3)	106·3 (7)	O(1)—C(1)—C(5)	114·4 (3)
C(2)—C(1)—C(5)	128·4 (4)	C(6)—C(5)—C(10)	117·8 (5)
C(1)—C(5)—C(6)	120·8 (6)	C(5)—C(6)—C(7)	121·3 (7)
C(6)—C(7)—C(8)	120·4 (6)	C(7)—C(8)—C(9)	119·8 (6)
C(8)—C(9)—C(10)	119·2 (6)	C(9)—C(10)—C(5)	121·5 (5)
C(10)—C(5)—C(1)	121·4 (4)	C(1)—C(2)—C(11)	120·9 (4)
C(2)—C(11)—C(12)	122·2 (5)	C(11)—C(12)—C(13)	120·5 (5)
C(12)—C(13)—C(14)	121·5 (6)	C(13)—C(14)—C(15)	118·9 (6)
C(14)—C(15)—C(16)	119·8 (6)	C(15)—C(16)—C(11)	122·1 (5)
C(16)—C(11)—C(12)	117·3 (5)	C(16)—C(11)—C(2)	120·5 (4)
C(11)—C(2)—C(17)	115·7 (3)	C(1)—C(2)—C(17)	123·1 (4)
C(2)—C(17)—C(18)	121·1 (4)	C(17)—C(18)—C(19)	122·5 (5)
C(18)—C(19)—C(20)	121·1 (5)	C(19)—C(20)—C(23)	121·1 (5)
C(19)—C(20)—C(21)	118·1 (5)	C(21)—C(20)—C(23)	120·9 (5)
C(20)—C(21)—C(22)	120·7 (5)	C(21)—C(22)—C(17)	120·6 (5)
C(2)—C(17)—C(22)	121·8 (5)	C(18)—C(17)—C(22)	116·9 (5)

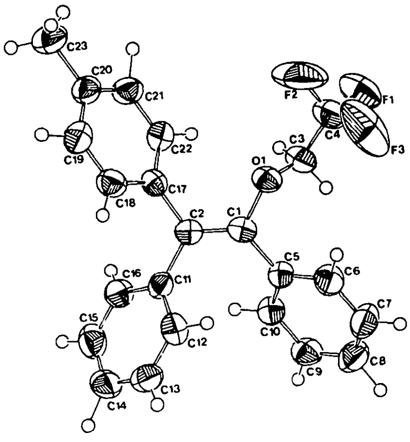

Fig. 1. *ORTEP*II (Johnson, 1976) view of the molecule with 50% probability ellipsoids.

---

[*] Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42942 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

in agreement with the conclusion of Osawa & Musso (1982) that the double bond in crowded ethylenes is highly resistant to elongation; the longest recorded lengths are 1·358 ± 0·004 Å. The C(1)—O(1) bond length of 1·416 (5) Å is also similar to those in other enols and enol ethers (Biali & Rappoport, 1984; Kaftory, Biali & Rappoport, 1985).

Financial support from the Canadian International Development Agency to YL and an operating grant from the Natural Sciences and Engineering Research Council of Canada to RJB, BER and CCL are gratefully acknowledged.

References

BIALI, S. E. & RAPPOPORT, Z. (1984). *J. Am. Chem. Soc.* **106**, 477–496.

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.

JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

KAFTORY, M., APELOIG, Y. & RAPPOPORT, Z. (1985). *J. Chem. Soc. Perkin Trans.* 2, pp. 29–37.

KAFTORY, M., BIALI, S. E. & RAPPOPORT, Z. (1985). *J. Am. Chem. Soc.* **107**, 1701–1709.

LEE, C. C. & WANIGASEKERA, D. (1986). *Can. J. Chem.* In the press.

OSAWA, E. & MUSSO, H. (1982). *Top. Stereochem.* **13**, 117–193.

STEWART, J. M. & HALL, S. R. (1984). The *XTAL* system. Tech. Rep. TR-873.2. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1986). C**42**, 1222–1225

Bond Length and Reactivity: The Beckmann Rearrangement. 1. Structure of Cyclopentanone *O*-(3,5-Dinitrobenzoyl)oxime *n*-Hexane Solvate (4:1)

BY PETER G. JONES

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany

AND MARTIN R. EDWARDS AND ANTHONY J. KIRBY

University Chemical Laboratory, Cambridge CB2 1EW, England

(*Received* 14 *November* 1985; *accepted* 15 *March* 1986)

Abstract. $C_{12}H_{11}N_3O_6.\frac{1}{4}C_6H_{14}$, $M_r = 314·79$, triclinic, $P\bar{1}$, $a = 10·712$ (3), $b = 11·297$ (3), $c = 13·050$ (3) Å, $\alpha = 74·63$ (2), $\beta = 76·78$ (2), $\gamma = 87·52$ (2)°, $V = 1482·1$ Å^3, $Z = 4$, $D_x = 1·41$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1$ cm^{-1}, $F(000) = 658$, $T = 291$ K, $R = 0·063$ for 4173 unique observed reflections. The two independent molecules differ only in the cyclopentane ring conformations. The N—O bond is lengthened with respect to free oximes by *ca* 0·055 Å. The hexane of solvation is well ordered and adopts a fully extended conformation. There are no unusually short contacts involving the solvent.

Introduction. Arising from our extensive investigations into the relationship between the length of a bond in the crystal and the rate at which it is broken in solution (Jones & Kirby, 1984), we have become increasingly interested in the geometrical consequences of the bond-lengthening effects we observe. Increasing electron withdrawal in the group *X* in a series of structures *R*—O*X* is associated with increasing *R*—O bond lengths, and the evidence is strong that this results from an increasingly important contribution to the ground-state structure from the valence tautomeric form R^+ $^-$O*X* (Allen & Kirby, 1984). If positive charge is indeed generated on the group *R*, it should in principle be possible to identify secondary changes induced by the need to accommodate that charge. Further, since it is precisely these changes which lead to classical ionic reactions in solution, the technique of the 'variable oxygen probe' (Jones & Kirby, 1984) offers the intriguing prospect of observing what happens in the early stages of suitable reactions. This paper reports the first of a series of crystal-structure determinations designed to apply this technique to a geometrically simple rearrangement reaction, the Beckmann rearrangement (review, Donaruma & Heldt, 1960).

The reaction involves the migration of the *E* substituent of a ketoxime derivative (1); no intermediate before the *N*-alkylnitrilium cation (2) has been detected, so the migration of the alkyl group is probably concerted with the departure of *X*O$^-$. The question of immediate interest is whether the extensive geometrical changes involved have proceeded to a measurable extent in suitable oxime derivatives, where *X*O$^-$ is the best leaving group consistent with a stable crystalline compound.