Structure of 1-Benzyl-2,2,3,3-tetramethyl-1-phenylphosphetanium Bromide, a Cyclobutane Derivative

By J. A. Campbell* and R. Larsen

Department of Chemistry, Montana State University, Bozeman, Montana 59715, USA

C. Campana

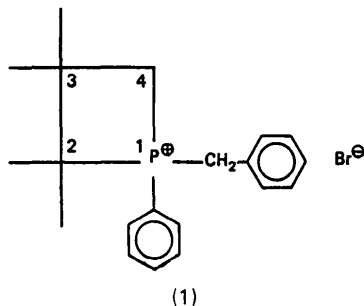*Nicolet Analytical Instruments, Madison, Wisconsin 53711, USA*

and S. E. Cremer

Department of Chemistry, Marquette University, Milwaukee, Wisconsin 53233, USA

Abstract. $C_{20}H_{26}P^+.Br^-$, $M_r = 376\cdot88$, monoclinic, $P2_1$, $a = 9\cdot596$ (2), $b = 9\cdot853$ (6), $c = 10\cdot252$ (7) Å, $\beta = 102\cdot59$ (3)°, $V = 946\cdot12$ Å^3, $Z = 2$, $D_m = 1\cdot32$, $D_x = 1\cdot34$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0\cdot71069$ Å, $\mu = 23\cdot7$ cm^{-1}, $F(000) = 392$, $T = 295$ K, $R = 0\cdot033$ for 1613 observed reflections. The four-membered ring is puckered with an angle of $28\cdot1°$, and the P—C bond distances are $1\cdot849$ (4), $1\cdot778$ (4), $1\cdot812$ (5), and $1\cdot801$ (3) Å. The bond angles around P vary from $81\cdot1$ (2) to $119\cdot5$ (2)°. The geometry around P is as expected in a four-membered ring.

Introduction. The geometry and ring puckering of cyclobutane derivatives have attracted considerable attention (Allen, 1984). Since conformational preferences in heterocyclic systems frequently do not run parallel to their hydrocarbon analogues (Quin, 1981), we have had a continuing interest in the geometry and conformational properties of phosphetane derivatives (Fitzgerald, Campbell, Smith, Caughlan & Cremer, 1978; Gray, Cremer & Marsi, 1976; Campbell, Caughlan, Fitzgerald, Campana & Cremer, 1984). We now describe the X-ray crystal structure of the title compound, (1), BTPB. The preparation of BTPB has been described by Cremer, Trivedi & Weitl (1971).

(1)

* Address all correspondence to this author. Present address: Battelle-Northwest, Box 999, Richland, WA 99352, USA.

Experimental. D_m by flotation in ethanol and methyl iodide, colorless crystals of BTPB suitable for X-ray analysis obtained by recrystallization from acetonitrile. Crystal size $0\cdot1 \times 0\cdot1 \times 1\cdot1$ mm, Nicolet *R*3*m* diffractometer, graphite monochromator (Campana, 1981), Mo $K\alpha$ radiation, precise cell dimensions obtained from least-squares refinement of 25 reflections (θ range 10–15°), three standard reflections (004, 060, 500) measured every 120 min, average intensity variation <3%. Range of *hkl*: $-13 \leq h \leq 13$, $0 \leq k \leq 13$, $0 \leq l \leq 14$, data collected by θ–2θ scan, 2928 data measured ($3 < 2\theta < 60°$), 1613 reflections considered observed with $I \geq 2\sigma(I)$, Lorentz, polarization, and absorption corrections, time decay ignored. Absorption corrections by numerical Gaussian integration method from crystal dimensions and indexed faces; max. and min. transmission coefficients $0\cdot82$ and $0\cdot71$, respectively. Br$^-$ position from Patterson map, full-matrix least squares, $\sum w(|F_o| - |F_c|)^2$ minimized where $w = [1/\sigma^2(F) + G(F)^2]$ where $G = 0\cdot001$; non-H atoms anisotropic, H atoms located in ΔF map, idealized coordinates not refined, isotropic thermal parameters for H assigned as $0\cdot06$ Å^2, 201 refined parameters, $R = 0\cdot033$, $wR = 0\cdot046$, scattering factors for P, C, Br, and H from *International Tables for X-ray Crystallography* (1962), $S = 1\cdot31$. Final $(\Delta/\sigma)_{max} = 0\cdot009$, final difference map showed no peaks or depressions larger than $0\cdot2$ e Å^{-3}. Calculations carried out with *SHELXTL* package of Nicolet *R*3*m* crystallographic system (Sheldrick, 1980).

Discussion. The final atomic parameters are given in Table 1,† and the structure and numbering scheme are

† Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43386 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

shown in Fig. 1. Table 2 is a listing of selected interatomic distances and angles with their standard deviations.

All phosphetane ring structures determined to date exhibit puckering of the four-membered ring. The amount of puckering is defined as the angle between the planes C(4)—P—C(2) and C(2)—C(3)—C(4) and is 28·1° for the title compound. Qualitatively, the amount of puckering has been related to the number of substituent interactions, specifically methyl–methyl interactions (Fitzgerald et al., 1978). An interaction is considered to exist between substituents which are attached to adjacent ring atoms and are cis to one

Table 1. *Atomic coordinates* $(\times 10^4)$ *and equivalent isotropic coefficients* $(\text{Å}^2 \times 10^3)$

	x	y	z	U_{eq}*
Br	2077 (1)	0	1385 (1)	63 (1)
P	1783 (1)	5576 (1)	1910 (1)	37 (1)
C(1)	1907 (5)	6591 (5)	−557 (4)	59 (2)
C(2)	2844 (4)	5844 (4)	627 (3)	43 (1)
C(3)	2816 (5)	4246 (5)	464 (5)	45 (2)
C(4)	1482 (4)	3981 (4)	1085 (4)	42 (1)
C(5)	2649 (5)	3763 (6)	−977 (4)	58 (1)
C(6)	4132 (5)	3570 (5)	1312 (4)	52 (1)
C(7)	4309 (5)	6514 (5)	1032 (5)	55 (2)
C(8)	233 (4)	6630 (5)	1899 (4)	49 (1)
C(9)	−544 (4)	6112 (4)	2938 (4)	45 (1)
C(10)	−1532 (5)	5093 (7)	2619 (4)	58 (2)
C(11)	−2201 (6)	4553 (10)	3567 (5)	81 (2)
C(12)	−1893 (6)	5052 (8)	4851 (6)	79 (2)
C(13)	−899 (6)	6033 (7)	5187 (5)	74 (2)
C(14)	−217 (5)	6606 (6)	4218 (5)	61 (2)
C(15)	2796 (4)	5455 (5)	3605 (3)	42 (1)
C(16)	2708 (5)	4314 (6)	4339 (4)	59 (2)
C(17)	3462 (7)	4236 (8)	5645 (5)	74 (2)
C(18)	4347 (5)	5297 (9)	6173 (4)	79 (2)
C(19)	4424 (6)	6452 (9)	5469 (5)	82 (2)
C(20)	3635 (5)	6563 (7)	4137 (5)	63 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.
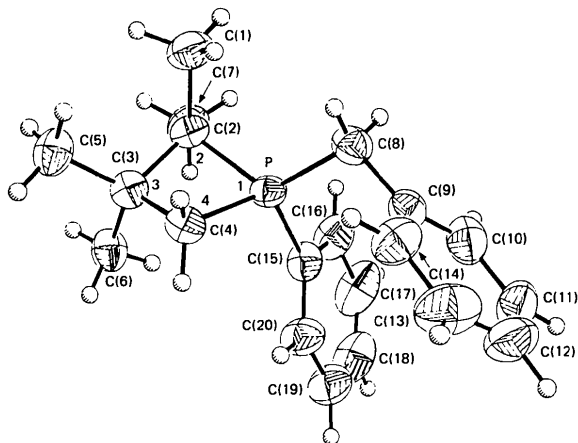

Fig. 1. The structure and numbering scheme for $C_{20}H_{26}P^+$. Non-H atoms are represented as thermal ellipsoids scaled to enclose 50% probability. The H atoms are represented as spheres with 0·15 Å radius.

Table 2. *Bond lengths* (Å) *and angles* (°)

P—C(2)	1·849 (4)	P—C(4)	1·778 (4)
P—C(8)	1·812 (5)	P—C(15)	1·801 (3)
C(1)—C(2)	1·532 (6)	C(2)—C(3)	1·583 (7)
C(2)—C(7)	1·526 (6)	C(3)—C(4)	1·570 (7)
C(3)—C(5)	1·527 (7)	C(3)—C(6)	1·522 (6)
C(8)—C(9)	1·516 (6)	C(9)—C(10)	1·370 (7)
C(9)—C(14)	1·371 (6)	C(10)—C(11)	1·382 (9)
C(11)—C(12)	1·376 (9)	C(12)—C(13)	1·349 (9)
C(13)—C(14)	1·420 (8)	C(15)—C(16)	1·366 (7)
C(15)—C(20)	1·396 (7)	C(16)—C(17)	1·378 (6)
C(17)—C(18)	1·381 (10)	C(18)—C(19)	1·358 (11)
C(19)—C(20)	1·414 (6)		
C(1)—C(2)—C(7)	110·7 (4)	C(1)—C(2)—C(3)	113·6 (3)
C(2)—P—C(8)	119·5 (2)	C(2)—P—C(4)	81·1 (2)
C(2)—C(3)—C(4)	96·8 (4)	C(2)—C(3)—C(5)	114·0 (4)
C(2)—P—C(15)	115·5 (2)	C(2)—C(3)—C(6)	112·5 (4)
C(3)—C(4)—P	89·1 (3)	C(3)—C(2)—C(7)	116·9 (4)
C(4)—P—C(8)	117·1 (2)	C(4)—P—C(15)	113·5 (2)
C(4)—C(3)—C(5)	114·7 (4)	C(4)—C(3)—C(6)	110·2 (4)
C(5)—C(3)—C(6)	108·4 (4)	P—C(2)—C(6)	108·3 (3)
P—C(2)—C(3)	86·2 (3)	C(8)—P—C(15)	108·3 (2)
P—C(2)—C(7)	119·0 (3)	P—C(8)—C(9)	109·4 (3)
C(8)—C(9)—C(10)	120·0 (4)	C(8)—C(9)—C(14)	120·6 (4)
C(10)—C(9)—C(14)	119·4 (4)	C(9)—C(10)—C(11)	121·2 (5)
C(10)—C(11)—C(12)	119·9 (7)	C(11)—C(12)—C(13)	119·5 (6)
C(12)—C(13)—C(14)	121·0 (5)	C(9)—C(14)—C(13)	118·9 (5)
P—C(15)—C(16)	120·1 (3)	P—C(15)—C(20)	118·0 (4)
C(16)—C(15)—C(20)	121·9 (4)	C(15)—C(16)—C(17)	120·0 (5)
C(16)—C(17)—C(18)	119·1 (6)	C(17)—C(18)—C(19)	121·7 (4)
C(18)—C(19)—C(20)	119·9 (6)	C(15)—C(20)—C(19)	117·3 (6)

another with respect to the phosphetane ring system. In view of this definition, BTPB has two cis methyl–methyl interactions. The C(1)—C(5) distance is 2·930 (3) Å and the C(6)—C(7) distance is 2·923 (4) Å, both of which are less than the sum of van der Waals radii (Bondi, 1964). Fitzgerald et al. (1978) found the puckering in the range of 19·6–24° for similar compounds with two cis methyl–methyl interactions. For BTPB, there is another cis interaction to consider, and the C(1)—C(8) distance is 3·269 (4) Å which is also less than the sum of van der Waals radii (Bondi, 1964). As the substituents on P become large, the cis interactions between the substituents on P and the substituents on adjacent C atoms become important. The puckering exhibited in BTPB may, in fact, represent an upper limit for compounds with two cis methyl–methyl interactions. Mazhar-ul-Haque, Ahmed & Horne (1985) have recently concluded that the difference in puckering is not significant between unsymmetrically and symmetrically substituted phosphetanes.

The following conformers may be considered with respect to puckering or conformational preference for BTPB.

(1A)   (1B)
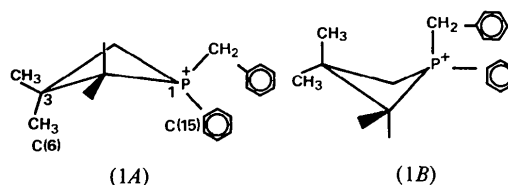
BTPB exists in the form (1*A*) and the distances C(6)—C(15) of 3·455 (6) Å and C(5)—C(8) of 5·005 (7) Å agree well with those of similar compounds in which C(3) is disubstituted (Fitzgerald *et al.*, 1978). The geometry around P in BTPB is as expected in a four-membered ring. The internal angle at P is 81·1 (2) with adjacent angles 86·2 (1) and 89·1 (3)°, and the internal angle opposite P is 96·8 (2)°. These angles match very well with those found in other substituted phosphetanes. Bond lengths and angles are comparable with the observed values in related structures.

References

ALLEN, F. H. (1984). *Acta Cryst.* C40, 65–77.
BONDI, A. (1964). *J. Phys. Chem.* 68, 441–448.

CAMPANA, C. F. (1981). *Nicolet P3/R3 Data Collection Manual.* Nicolet Analytical Instruments, Madison, Wisconsin.
CAMPBELL, J. A., CAUGHLAN, C. N., FITZGERALD, A. F., CAMPANA, C. F. & CREMER, S. E. (1984). *Acta Cryst.* C40, 1918–1920.
CREMER, S. E., TRIVEDI, B. C. & WEITL, F. L. (1971). *J. Org. Chem.* 36, 3226–3231.
FITZGERALD, A., CAMPBELL, J. A., SMITH, G. D., CAUGHLAN, C. N. & CREMER, S. E. (1978). *J. Org. Chem.* 43, 3513–3517.
GRAY, G. A., CREMER, S. E. & MARSI, K. L. (1976). *J. Am. Chem. Soc.* 98, 2109–2119.
International Tables for X-ray Crystallography (1962). Vol. III, 2nd ed. Birmingham: Kynoch Press. (Present distributor D. Reidel, Dordrecht.)
MAZHAR-UL-HAQUE, AHMED, J. & HORNE, W. (1985). *Acta Cryst.* C41, 975–977.
QUIN, L. D. (1981). In *The Heterocyclic Chemistry of Phosphorus.* New York: John Wiley.
SHELDRICK, G. M. (1980). *Nicolet SHELXTL Structure Determination Manual.* Nicolet Analytical Instruments, Madison, Wisconsin.

4-Benzylidene-2,3,4,5-tetrahydro-1-benzoxepin-5-one

BY A. KATRUSIAK, M. RATAJCZAK-SITARZ AND Z. KAŁUSKI

Department of Chemistry, Adam Mickiewicz University, Grunwaldzka 6, 60–780 Poznań, Poland

AND V. D. ORLOV, U. A. BOROVOI AND E. I. MIHEDKINA

Department of Organic Chemistry, M. Gorkii University, Kharkov, USSR

Abstract. $C_{17}H_{14}O_2$, $M_r = 250·3$, orthorhombic, $P2_12_12_1$, $a = 11·208$ (1), $b = 12·828$ (2), $c = 8·987$ (1) Å, $V = 1292·1$ (3) Å^3, $Z = 4$, $D_x = 1·290$ (6) g cm^{-3}, $\lambda(\text{Cu }K\alpha) = 1·54178$ Å, $\mu(\text{Cu }K\alpha) = 5·82$ cm^{-1}, $F(000) = 528$, $T = 292$ K, $R = 0·047$ for 992 unique reflections. The tetrahydrooxepin ring is in a twist-boat conformation. The conformation of the *cisoid* 1,3-enone bridge between the two phenyl rings is modified from that in 3-benzylidene-4-chromanone by the tetrahydrooxepin ring. The inclination angle between the two planar phenyl rings is 20·2 (5)°.

Introduction. The present investigation is a continuation of our previous X-ray studies of α,β-unsaturated ketones (Katrusiak, Ratajczak-Sitarz, Kałuski & Orlov, 1987, and references cited therein). 4-Benzylidene-tetrahydrooxepinone [hereinafter referred to as (I)] distinguishes itself from the ketones investigated previously by its seven-membered tetrahydrooxepin ring, which introduces strains in the molecular skeleton and modifies its conformation. The detailed spectroscopic studies of (I) and its analogues have been reported by

Orlov, Borovoi & Lavrushin (1976) and Orlov, Mihedkina & Shandula (1984).

Experimental. Recrystallization from ethanol as colourless prisms, crystal fragment 0·40 × 0·31 × 0·21 mm, Syntex $P2_1$ diffractometer, graphite-monochromated Cu $K\alpha$ radiation. Unit cell from least-squares fit to 15 reflections ($13 \le 2\theta \le 29°$); 2θ–θ mode, variable scan speed: 2·0 to 29·3° min^{-1}, two control reflections monitored every 50 measurements; 1027 reflections measured up to $2\theta = 115°$; index range h 0/12, k 0/13 and l 0/9; profile analysis method of Lehmann & Larsen (1974), 993 independent reflections ($R_{int} = 0·025$) with $I \ge 1·96\sigma_I$; Lp corrections. Structure solved with *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980); H atoms from difference Fourier map, only their isotropic temperature factors were initially refined, but then fixed in the final cycles. The structure refinements were carried out for both enantiomorphs – the presented enantiomorph was chosen in the test of the R-factor ratio: $\mathscr{R} = wR_q/wR_0 = 1·164$ compared to $\mathscr{R}_{171,820,0.01} = 1·153$