Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
O(1)	−0.6156 (3)	0.1781 (2)	−0.5425 (2)	0.0628 (7)
O(2)	−0.5475 (3)	−0.2623 (1)	−0.6902 (2)	0.0678 (7)
O(3)	−0.9112 (3)	0.0544 (2)	−0.8027 (2)	0.0934 (9)
N(1)	−0.6882 (3)	0.0415 (2)	−0.6802 (2)	0.0436 (6)
N(4)	−0.4530 (3)	−0.1134 (2)	−0.5782 (2)	0.0531 (8)
C(2)	−0.5872 (4)	0.0851 (2)	−0.5914 (2)	0.0448 (8)
C(3)	−0.4345 (4)	0.0127 (3)	−0.5560 (3)	0.0490 (9)
C(5)	−0.5440 (4)	−0.1561 (2)	−0.6658 (2)	0.0482 (9)
C(6)	−0.6436 (4)	−0.0707 (2)	−0.7387 (2)	0.0470 (9)
C(7)	−0.8301 (4)	0.1030 (3)	−0.7280 (3)	0.058 (1)
C(8)	−0.8776 (6)	0.2240 (4)	−0.6881 (4)	0.069 (1)
C(9)	−0.2702 (5)	0.0643 (4)	−0.6047 (4)	0.065 (1)
C(10)	−0.3473 (7)	−0.1946 (4)	−0.5087 (4)	0.078 (1)
C(11)	−0.5498 (6)	−0.0496 (3)	−0.8522 (3)	0.060 (1)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

O(1)—C(2)	1.213 (3)	N(1)—C(7)	1.418 (4)
O(2)—C(5)	1.231 (3)	N(4)—C(5)	1.331 (3)
N(1)—C(2)	1.389 (3)		
C(2)—N(1)—C(6)	120.8 (2)	N(4)—C(3)—C(2)	113.9 (3)
C(3)—N(4)—C(5)	122.9 (2)	N(4)—C(5)—C(6)	118.5 (2)
N(1)—C(2)—C(3)	117.5 (2)	N(1)—C(6)—C(5)	114.3 (2)

Table 3. *Torsion angles* (°)

C(2)—N(1)—C(6)—C(5)	φ_1	27.1 (3)
C(5)—N(4)—C(3)—C(2)	φ_2	31.3 (4)
N(1)—C(6)—C(5)—N(4)	ψ_1	−24.1 (4)
N(4)—C(3)—C(2)—N(1)	ψ_2	−27.2 (4)
C(3)—C(2)—N(1)—C(6)	ω_1	−1.3 (3)
C(6)—C(5)—N(4)—C(3)	ω_2	−5.2 (4)

The θ-scan width used was $(0.80 + 0.3\tan\theta)°$ at a speed of $8.0°\ \mathrm{min}^{-1}$ in ω. The weak reflections were rescanned a maximum of 4 times and the counts accumulated to ensure good counting statistics. Stationary background counts were made on each side of the reflection with a 2:1 ratio of peak to background counting time. The structure was solved by direct methods and expanded using Fourier techniques (Beurskens *et al.*, 1992).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SAPI91* (Fan, 1991). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1020). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Benedetti, E., Marsh, R. E. & Goodman, M. (1976). *J. Am. Chem. Soc.* **98**, 6676–6684.

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., Garcia-Granda, S., Gould, R. O., Smits, J. M. M. & Smykalla, C. (1992). *The DIRDIF Program System*. Technical Report. Crystallography Laboratory, Univ. of Nijmegen, The Netherlands.

Fan, H.-F. (1991). *SAPI91. Structure Analysis Programs with Intelligent Control.* Rigaku Corporation, Tokyo, Japan.

Filhol, A. & Timmins, P. A. (1976). *Acta Cryst.* B**32**, 3116–3118.

Hooker, T. M., Bayley, P. M., Radding, W. & Schellman, J. A. (1974). *Biopolymers*, **13**, 549–566.

IUPAC–IUB Commission on Biochemical Nomenclature (1970). *Biochemistry*, **9**, 3471–3479.

Karle, I. L. (1981). *The Peptides*, Vol 4, edited by E. Gross & J. Meienhofer, pp. 4–8. New York: Academic Press.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1992). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.6c. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Slater, G. P. (1969). *Chem. Ind.* p. 1092.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558–564.

Acta Cryst. (1995). C**51**, 1838–1841

cis-3-Hydroxytricyclo[7.5.0.0^{3,8}]tetradec-1(9)-en-2-one

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Abstract

The stereochemistry at the single-bond ring junction in the title compound, $C_{14}H_{20}O_2$, indicates that in the transposition reaction leading to its formation the most stable *cis* product is produced. The cycloheptene ring is disordered over two positions related by a pseudo-mirror perpendicular to the ring-junction double bond. The hydroxyl group is involved in an intermolecular hydrogen bond.

Comment

As part of our research program dealing with the synthesis of polycyclic cyclopentane derivatives, we considered reactions of the type shown below, the mechanism of which has been reported elsewhere (Jamart-

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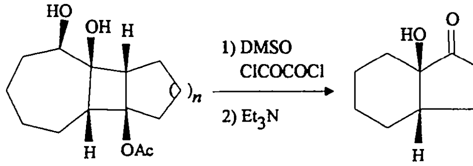
Grégoire, Brosse, Ianelli, Nardelli & Caubère, 1993; Brosse, Jamart-Grégoire & Caubère, 1995).



(1) (2)

The stereochemistry at the single-bond ring junction of (2) ($n = 3$) could not be defined either from the usual spectroscopic data or by correlation of the starting materials and the transposed products. The X-ray crystal structure analysis of (2) was therefore carried out. The structure of the starting material (1) ($n = 2$) has been determined previously (Ianelli, Nardelli, Belletti, Brosse, Jamart-Grégoire & Caubère, 1993).

From Fig. 1, which shows an *ORTEP* (Johnson, 1965) drawing of the title molecule, it appears that the transposition reaction proceeded in such a way that the more stable *cis* product was obtained. The molecule is built up of three fused rings, *i.e.* cyclopentenone (*A*), cyclohexane (*B*) and cycloheptene (*C*), the last being disordered over two positions related approximately by a local pseudo-mirror running between atom C12 and the midpoint of the double bond. Fig. 2 compares the geometry of the cycloheptene ring in the two positions, $C_{\rm I}$ and $C_{\rm II}$, showing that the model used to interpretate the disorder is quite reasonable.

The presence of three C_{sp^2} atoms causes a flattening of ring *A* [total puckering amplitude (Cremer & Pople, 1975): $Q_T(A) = 0.024\,(3)$ Å] and a tendency for ring *A* to be coplanar with ring *C* [$A/C_{\rm I} = 174.2\,(1)$, $A/C_{\rm II} = 175.6\,(1)°$]. Ring *B* is much more puckered [$Q_T(B) = 0.731\,(4)$ Å] with a twist conformation, as indicated by two local pseudo-mirrors, one running along the C3–C6 direction and the other along the midpoints of the C4—C5 and C2—C7 bonds. The mean plane through ring *B* forms a dihedral angle of 141.6 (1)° with that of the central ring *A*. Bond distances and angles (Table 2) are as expected.

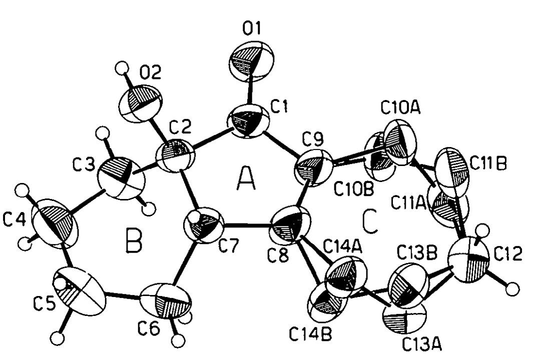


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecule of (2) with displacement ellipsoids at the 30% probability level. The H atoms of the disordered C10—C11 and C13—C14 ethylene groups are omitted for clarity.

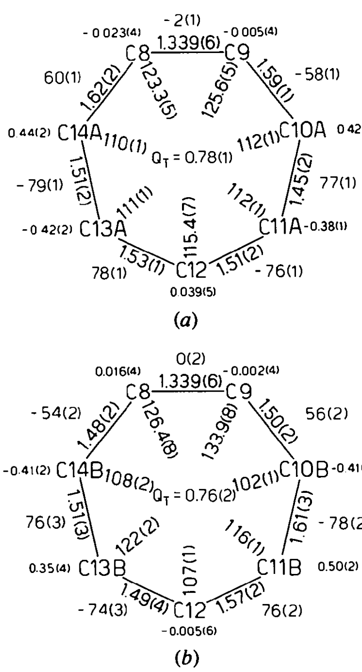


Fig. 2. Geometric parameters [bond distances (Å), angles (°), torsion angles (°), distances from the mean plane through the ring (Å) and total puckering amplitudes Q_T (Å)] describing the two rings generated by the disorder of cyclohexene.

The orientation of the hydroxyl H atom is determined by the hydrogen bond it forms with the keto O1 atom [$O2\cdots O1^{\rm i}$ 2.830 (4), $H2\cdots O1^{\rm i}$ 2.03 (4) Å, O2—$H2\cdots O1^{\rm i}$ 166 (4)°; symmetry code (i) $1 - x, -y, 1 - z$]. This interaction, together with van der Waals contacts, determines the nature of the packing in the crystal.

Experimental

Compound (2) ($n = 3$) was obtained by treating compound (1) ($n = 2$) with ClCOCOCl and DMSO at 203 K in CH_2Cl_2, followed by addition of Et_3N to the reaction mixture (see scheme above). Elemental analysis: found, C 76.39, H 9.23%; calculated for $C_{14}H_{20}O_2$, C 76.32, H 9.15%; calculated for $C_{14}H_{16}O_2$, C 77.75, H 7.46%. ^{1}H NMR (60 MHz, CCl_4) δ: 3.9–3.5 (*m*, 1H, OH), 2.8–1.0 p.p.m. (*m*, 19 H). ^{13}C NMR ($CDCl_3$) δ: 209.6 (C═O), 76.3 (C—OH), 49.3 (CH), 30.8, 30.7, 30.0, 26.1, 25.7, 23.0, 22.5, 19.5, 17.6 p.p.m. (9 × CH_2). IR (NaCl film) ν: 3600–3100 (OH), 1702 (C═O), 1633 cm^{-1} (C═C).

Crystal data

$C_{14}H_{20}O_2$
$M_r = 220.31$
Monoclinic
$P2_1/c$
$a = 9.402\,(4)$ Å
$b = 10.045\,(6)$ Å
$c = 13.658\,(6)$ Å
$\beta = 106.49\,(2)°$

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 29 reflections
$\theta = 17$–$36°$
$\mu = 0.608$ mm^{-1}
$T = 293\,(2)$ K
Tabular

$V = 1237$ (1) Å^3
$Z = 4$
$D_x = 1.183$ Mg m^{-3}

0.36 × 0.29 × 0.18 mm
Colourless

Data collection

Siemens AED diffractometer
$\theta/2\theta$ scans
Absorption correction: none
2471 measured reflections
2332 independent reflections
874 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.020$

$\theta_{\rm max} = 69.98°$
$h = -10 \rightarrow 11$
$k = -12 \rightarrow 10$
$l = -16 \rightarrow 8$
1 standard reflection monitored every 50 reflections
intensity variation: within statistical fluctuation

Refinement

Refinement on F^2
$R(F) = 0.0544$
$wR(F^2) = 0.1721$
$S = 1.291$
2332 reflections
189 parameters
$w = 1/[\sigma^2(F_o^2) + (0.1291P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.019$
$\Delta\rho_{\rm max} = 0.13$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.15$ e Å^{-3}

Extinction correction: $F_c^* = kF_c[1 + (0.001\chi \times F_c^2\lambda^3/\sin2\theta)]^{-1/4}$
Extinction coefficient: 0.003 (1)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
O1	0.6554 (3)	−0.1249 (3)	0.5241 (2)	0.1221 (11)
O2	0.5782 (3)	0.1043 (2)	0.3839 (2)	0.0909 (8)
C1	0.6884 (4)	−0.1065 (3)	0.4447 (2)	0.0873 (10)
C2	0.5973 (3)	−0.0283 (3)	0.3536 (2)	0.0752 (9)
C3	0.4493 (4)	−0.0976 (4)	0.3069 (3)	0.1043 (12)
C4	0.3672 (5)	−0.0320 (6)	0.2069 (3)	0.138 (2)
C5	0.4624 (6)	−0.0175 (5)	0.1338 (3)	0.133 (2)
C6	0.6147 (5)	−0.0795 (4)	0.1736 (3)	0.1060 (13)
C7	0.6938 (4)	−0.0263 (4)	0.2802 (2)	0.0808 (10)
C8	0.8280 (4)	−0.1060 (4)	0.3338 (3)	0.1092 (14)
C9	0.8238 (4)	−0.1523 (4)	0.4249 (3)	0.1063 (13)
C10*A*†	0.9600 (17)	−0.2148 (15)	0.5095 (8)	0.104 (4)
C10*B*‡	0.8931 (21)	−0.2696 (24)	0.4892 (15)	0.104 (5)
C11*A*†	1.0237 (15)	−0.3282 (14)	0.4721 (8)	0.115 (4)
C11*B*‡	1.0671 (18)	−0.2467 (28)	0.5013 (14)	0.114 (6)
C12	1.1203 (5)	−0.2865 (6)	0.4061 (4)	0.130 (2)
C13*A*†	1.0371 (18)	−0.2421 (15)	0.2976 (10)	0.115 (4)
C13*B*‡	1.0701 (23)	−0.1792 (46)	0.3287 (19)	0.156 (12)
C14*A*†	0.9776 (16)	−0.1027 (14)	0.2976 (8)	0.098 (3)
C14*B*‡	0.9104 (23)	−0.1649 (22)	0.2670 (14)	0.100 (5)

† Occupancy factor = 0.61 (2).
‡ Occupancy factor = 0.39 (2).

Table 2. *Selected geometric parameters* (Å, °)

O1—C1	1.224 (3)	C3—C4	1.516 (6)
O2—C2	1.421 (4)	C4—C5	1.525 (6)
C1—C9	1.449 (5)	C5—C6	1.514 (6)
C1—C2	1.516 (4)	C6—C7	1.532 (5)
C2—C3	1.525 (5)	C7—C8	1.498 (5)
C2—C7	1.531 (4)	C8—C9	1.339 (5)
O1—C1—C2	125.4 (3)	C6—C5—C4	113.4 (3)
O1—C1—C9	125.1 (3)	C5—C6—C7	110.6 (3)
C9—C1—C2	109.4 (3)	C2—C7—C6	113.6 (3)
O2—C2—C1	109.6 (2)	C8—C7—C2	104.3 (2)
O2—C2—C3	112.0 (3)	C8—C7—C6	113.1 (3)
O2—C2—C7	109.0 (3)	C9—C8—C7	113.4 (3)
C1—C2—C3	110.1 (3)	C7—C8—C14*A*	121.6 (5)
C1—C2—C7	104.0 (2)	C7—C8—C14*B*	115.4 (7)
C3—C2—C7	111.9 (3)	C1—C9—C8	108.8 (3)
C4—C3—C2	110.5 (3)	C1—C9—C10*A*	123.9 (5)
C3—C4—C5	112.8 (4)	C1—C9—C10*B*	113.4 (7)

The integrated intensities were obtained by a modified version (Belletti, Ugozzoli, Cantoni & Pasquinelli, 1979) of the Lehmann & Larsen (1974) peak-profile analysis procedure and corrected for standard Lorentz and polarization effects, but not for absorption.

The structure was solved by direct methods and refined by anisotropic full-matrix least squares for all the non-H atoms. The H atoms attached to atoms C3–C7 were found from a $\Delta\rho$ map, but only H7 was refined isotropically as a free atom, all the other atoms being placed in calculated positions, riding on their attached atoms. $U_{\rm iso}$ for H2 was refined, while those for the H atoms of the C3–C6 methylene groups were assumed to be $1.5U_{\rm eq}$ of the attached C atoms. A common U was refined for the H atoms of the disordered methylene groups and also for the H atoms attached to C12.

At first, disorder was not taken into account and the unsatisfactory nature of the results was attributed to the poor quality of the crystals. A second data collection, with a specimen from an independently prepared sample, gave results which were no better. The structure showed high thermal motion or disorder, particularly for the atoms of the C10—C11 and C13—C14 ethylene groups. Moreover, the shortness of the C10—C11 and C13—C14 bonds could have been taken to indicate multiple character, though this would not have been consistent with either the chemical analysis, the ^{1}H NMR, ^{13}C NMR and IR spectra, or the puckering of the ring, all of which indicated the presence of only one C═C double bond, *i.e.* at the ring junction. A model with the cyclohexene ring disordered over two positions, C8═C9—C10*A*—C11*A*—C12—C13*A*—C14*A* and C8═C9—C10*B*—C11*B*—C12—C13*B*—C14*B*, was therefore refined and it gave values of 0.61 (2) and 0.39 (2) for the occupancy factors of the two disordered groups.

Calculations were carried out on the ENCORE91 and GOULD-POWERNODE 6040 computers of the Centro di Studio per la Strutturistica Diffrattometrica del CNR (Parma), and on a COMPAQ-486c portable computer.

Data collection: local programs. Cell refinement: *LQPARM* (Nardelli & Mangia, 1984). Data reduction: local programs. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *PARST* (Nardelli, 1983) and *PARSTCIF* (Nardelli, 1991).

Financial support from the European Community Commission under contract NSC1000657 is gratefully acknowledged.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, torsion angles and contact distances have been deposited with the IUCr (Reference: MU1162). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Belletti, D., Ugozzoli, F., Cantoni, A. & Pasquinelli, G. (1979). *Gestione on Line di Diffrattometro a Cristallo Singolo Siemens AED con Sistema General Automation Jumbo* 220. Internal Report 1-3/79. Centro di Studio per la Strutturistica Diffrattometrica del CNR, Parma, Italy.

Brosse, N., Jamart-Grégoire, B. & Caubère, P. (1995). *Synth. Commun.* **25**, 157–165.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Ianelli, S., Nardelli, M., Belletti, D., Brosse, N., Jamart-Grégoire, B. & Caubère, P. (1993). *Acta Cryst.* C**49**, 2022–2027.

Jamart-Grégoire, B., Brosse, N., Ianelli, S., Nardelli, M. & Caubère, P. (1993). *J. Org. Chem.* **58**, 4572–4578.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Lehmann, M. S. & Larsen, F. K. (1974). *Acta Cryst.* A**30**, 580–589.

Nardelli, M. (1983). *Comput. Chem.* **7**, 95–98.

Nardelli, M. (1991). *PARSTCIF. Program for the Creation of a CIF from the Output of PARST*. Univ. of Parma, Italy.

Nardelli, M. & Mangia, A. (1984). *Ann. Chim. (Rome)*, **74**, 163–174.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.

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Two Trimethylphenylphosphonium Iodides

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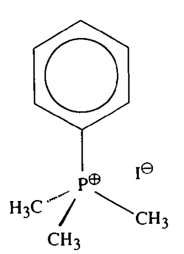
Abstract

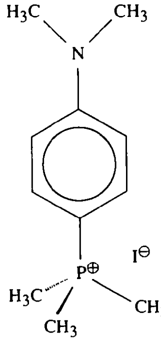
The structures of trimethylphenylphosphonium iodide, $C_9H_{14}P^+.I^-$, and (*p*-dimethylaminophenyl)trimethylphosphonium iodide, $C_{11}H_{19}NP^+.I^-$, have been determined at 100 K in order to study the substituent perturbation of the trimethylphosphonium group and the additional effect of a *p*-dimethylamino group. Trimethylphenylphosphonium iodide crystallizes in the orthorhombic space group $Pca2_1$ with two independent molecules in the asymmetric unit. The *p*-dimethylamino-substituted compound has a planar amino group with an N—C(phenyl) bond distance in the double-bond range. Both structures contain short C—H···I distances below the sum of the van der Waals radii.

Comment

Quaternary phosphonium salts and phosphabetaines are common reagents in the Wittig olefin synthesis. Phosphine oxides resulting from phosphonium salts can be removed as an insoluble complex with lithium halide in ether solution. For *p*-dimethylaminophenyl-substituted phosphonium salts, the separation of the resulting phosphine oxide is facilitated by utilization of their solubility in dilute acid (Trippett & Walker, 1961). Trimethylphenylphosphonium iodide, (I), was chosen in order to study its ring geometry and, consequently, the acceptor or donor effect of the trimethylphosphonium group, which is indicated by the deviation of the *ipso* angle from 120° (Domenicano, 1989). The structures of (I) and (*p*-dimethylaminophenyl)trimethylphosphonium iodide, (II), were determined. Only one trimethylphosphonium salt is reported in the Cambridge Structural Database (1992), the decachlorotantalate (Cotton & Najjar, 1981). However, the phenyl ring geometry was not determined exactly and, therefore, no conclusion is provided concerning substituent effects.



(I)



(II)

The phosphonium iodide (I) does not show any significant perturbation of the phenyl ring and, therefore, the trimethylphosphonium substituent exhibits neither a donor nor an acceptor effect. Insertion of the electron-donating *p*-dimethylamino group in (II) causes only a slight change in the ring geometry but a significant flattening of the N-atom environment. Both *ipso* angles are reduced [117.7 (2) and 117.6 (2)°] and the phenyl ring is elongated. The N—C(phenyl) bond length is 1.373 (3) Å and, therefore, within the double-bond range, whereas the P—C(phenyl) distance of 1.797 (6) Å represents a single bond. The sum of these structural changes suggests the existence of a substituent push–pull effect. Hence, our results are in satisfactory agreement with spectroscopic measurements (Schiemenz, 1964), which show only a small effect for compound (I) but a strong bathochromic effect after dimethylamino substitution. Views of (I) and (II) are shown in Figs. 1 and 2, respectively.

The packing of both crystal structures is dominated by short C—H···I contacts with a minimum distance of 2.99 (2) Å (Tables 3 and 6), about 0.35 Å lower than the sum of the van der Waals radii [$r(\mathrm{I}) + r(\mathrm{H}) = 2.15 + 1.20 = 3.35$ Å (Pauling, 1960)]. In both cases, the I^- ions are positioned almost symmetrically above the triangle formed by the trimethylphosphonium group, and one C—H bond of each methyl group is directed towards

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