

ent progressivement en phase anhydre orthorhombique (phase II).

Les nouveaux cristaux, de dimensions micro-métriques, restent agglomérés en formant des amas de couleur blanchâtre en pseudo-morphose des cristaux originels. De ce fait, il a été impossible d'isoler un monocristal de phase II qui soit de dimensions suffisantes pour effectuer une détermination structurale directe. Ces cristaux anhydres, replacés sous conditions de vapeur saturante à température ambiante, se réhydratent sans croissance des individus cristallins.

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Structural Study of Chromotropic [Dibenzofuran]diones by X-ray Structure Analysis and MO Calculation

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Abstract

The crystal structure of the benzene solvate of *meso*-3,3'-diphenyl-[3,3'-dibenzofuran]-2,2'-(3*H*,3'*H*)-dione (*Ia*), which exhibits mechanochromism and thermochromism, has been determined. Crystal data: $C_{28}H_{18}O_4 \cdot 0.5(C_6H_6)$, $M_r = 457.5$, triclinic, $P\bar{1}$, $a = 10.421$ (2), $b = 12.772$ (2), $c = 10.016$ (2) Å, $\alpha = 108.22$ (1), $\beta = 114.42$ (1), $\gamma = 72.35$ (1)°, $V = 1129.4$ (4) Å³, $Z = 2$, $D_x = 1.345$ g cm⁻³, $\lambda(Cu K\alpha) = 1.54184$ Å, $\mu = 0.67$ mm⁻¹, $T = 293$ K, $F(000) = 478.0$, $R = 0.060$ for 2369 observed reflections. The (*Ia*) molecule adopts an unsymmetrical *gauche* conformation in the crystal. The bond distance C(3)—C(3'), which undergoes homolytic cleavage by mechanical and thermal energy, is 1.596 (5) Å. Conformational analysis of (*Ia*) was performed by the PM3 methods to give a much shorter C(3)—C(3') distance (1.564 Å) in the optimized *gauche* form. According to the calculation, the *gauche* form and the centrosymmetric *anti* form are almost equal in energy, but variable-temperature NMR experiment suggests that (*Ia*) also exists in the *gauche* form in solution.

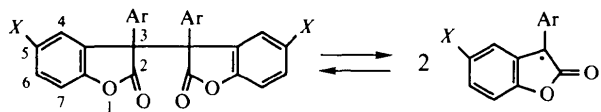
Introduction

meso-3,3'-Diphenyl-[3,3'-dibenzofuran]-2,2'-(3*H*,3'*H*)-dione (*Ia*) was reported to exhibit thermochromism

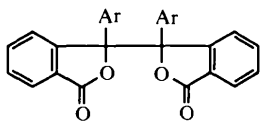
(Löwenbein & Simonis, 1924) and piezochromism in the solid state (Löwenbein & Schmidt, 1927). These chromotropic behaviors are due to homolysis of the C(3)—C(3') bond to give blue-colored radicals and recombination of the radicals into the colorless dimer (Watanabe, 1987). Recently we revealed that the piezochromic phenomena due to homolytic bond cleavage on (*Ia*) and other related compounds are caused by mechanical energy, such as rubbing and pressing rather than high pressure, and therefore, we proposed the term mechanochromism for this type of reversible color change (Ohkanda, Mori, Maeda & Osawa, 1992). It is expected that the bonds which are homolytically cleaved by applying rather small mechanical energy should be significantly lengthened. In fact, the C(3)—C(3') bond in (*Ib*), which also showed mechanochromism, was found to be 1.624 Å by the X-ray method (Mori, Kubota, Watanabe & Maeda, 1994).

On the other hand, *meso*-3,3'-diphenyl-3,3'-biphtalidyl (*IIa*), an isomer of (*Ia*), which was prepared through dimerization of phthalidyl radicals (Bhatt, Kamath & Ravindranathan, 1971), did not undergo homolysis of C(3)—C(3') under conditions where (*Ia*) and (*Ib*) underwent thermal and mechanochemical radical dissociation. In order to clarify the relationship between molecular structure of the dimer and homolytic cleavage of the central bond,

we have determined the crystal structure of (Ia) and also performed conformational analyses for (Ia), (Ib) and (IIa) by PM3 methods.



(Ia): X = H, Ar = Ph
 (Ib): X = Cl, Ar = Ph
 (Ic): X = H, Ar = 4-ClC₆H₄



(IIa): Ar = Ph
 (IIb): Ar = *p*-BrC₆H₄

Experimental

(Ia) was synthesized using the method of Löwenbein & Simonis (1924). A colorless plate-like crystal with the dimensions 0.3 × 0.25 × 0.1 mm was obtained by recrystallization from benzene-ethanol. Cell parameters were refined by the least-squares of 22 independent 2θ values ($54 < 2\theta < 57^\circ$) on a Rigaku AFC-7R four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation at 293 K. The intensity data were collected up to $2\theta = 120^\circ$ by an ω - 2θ scan technique with a scan width of $(1.84 + 0.4 \tan \theta)^\circ$ and a scan speed of 8° min^{-1} in θ . The intensities of three standard reflections were monitored every 150 reflections and no significant variation was observed ($< 2\%$). 3571 reflections were measured, of which 2929 were unique ($R_{\text{int}} = 0.05$). 2369 reflections with $|F_o| > 2\sigma(|F_o|)$ were considered as observed and used for structure determination. Data were corrected for Lorentz and polarization factors but not for absorption. The structure was solved by direct methods using *MULTAN78* (Main *et al.*, 1978). Weighted Fourier calculations showed the existence of three additional peaks, which could be assigned to the C atoms of the benzene molecule. Refinements were made by full-matrix least squares methods with *SHELX76* (Sheldrick, 1976). Some H atoms were located from difference maps and other H-atom positions were calculated geometrically and then refined. The atoms in the benzene molecule were disordered between two sets of positions and the C atoms were refined isotropically with occupancy factors fixed at 0.5; H atoms were not included. A final refinement, with anisotropic for non-H atoms in (Ia) and isotropic thermal parameters for H atoms, was converged at $R = 0.060$ and $wR = 0.062$ for 2369 observed reflections and 385 refined parameters. The weighting scheme was $w = 1/[\sigma^2(|F_o|) + 0.001|F_o|^2]$. The final difference map showed $-0.21 < \Delta\rho < 0.37 \text{ e } \text{Å}^{-3}$. The final atomic coordinates are listed in

Table 1. Final atomic coordinates ($\times 10^4$) for (Ia) and equivalent isotropic thermal parameters with their estimated standard deviations for non-H atoms

$$B_{\text{eq}} = (4/3)\sum_i \sum_j \beta_{ij} a_i a_j$$

	x	y	z	B_{eq}
O(1)	5184 (3)	8778 (2)	219 (3)	4.4 (1)
C(2)	4579 (4)	8353 (3)	-1288 (4)	3.8 (2)
C(3)	3332 (3)	7797 (3)	-1570 (4)	3.0 (1)
C(4)	3241 (3)	8147 (3)	-23 (4)	2.9 (1)
C(5)	2302 (4)	8048 (3)	564 (4)	3.4 (1)
C(6)	2536 (4)	8447 (3)	2081 (4)	3.9 (2)
C(7)	3695 (4)	8951 (3)	3021 (5)	4.3 (2)
C(8)	4629 (5)	9076 (3)	2456 (4)	4.3 (2)
C(9)	4373 (4)	8674 (3)	954 (4)	3.4 (1)
O(10)	4995 (3)	8451 (2)	-2163 (3)	4.9 (1)
C(11)	3801 (4)	6500 (3)	-2042 (4)	3.8 (1)
C(12)	3340 (5)	5804 (3)	-1612 (5)	4.9 (2)
C(13)	3754 (6)	4641 (4)	-1985 (6)	6.5 (2)
C(14)	4658 (7)	4182 (5)	-2777 (7)	7.2 (2)
C(15)	5153 (6)	4848 (5)	-3194 (7)	7.4 (3)
C(16)	4725 (5)	6026 (4)	-2839 (6)	5.7 (2)
O(1')	2013 (3)	9190 (2)	-4587 (3)	4.6 (1)
C(2')	2195 (4)	8175 (4)	-4248 (4)	4.1 (2)
C(3')	1947 (4)	8364 (3)	-2777 (4)	3.1 (1)
C(4')	1726 (4)	9646 (3)	-2299 (4)	3.1 (1)
C(5')	1533 (4)	10417 (3)	-1044 (4)	3.5 (1)
C(6')	1330 (4)	11561 (3)	-971 (5)	4.5 (2)
C(7')	1338 (5)	11918 (4)	-2136 (6)	5.1 (2)
C(8')	1562 (2)	11171 (4)	-3374 (6)	4.7 (2)
C(9')	1754 (4)	10036 (3)	-3412 (4)	3.8 (1)
O(10')	2466 (3)	7316 (3)	-5094 (3)	5.5 (1)
C(11')	589 (4)	7918 (3)	-3151 (4)	3.1 (1)
C(12')	-505 (4)	8562 (3)	-2623 (4)	3.6 (1)
C(13')	-1749 (4)	8181 (4)	-3011 (5)	4.4 (2)
C(14')	-1924 (5)	7156 (4)	-3958 (5)	4.8 (2)
C(15')	-865 (5)	6508 (3)	-4500 (5)	5.0 (2)
C(16')	393 (4)	6868 (3)	-4107 (4)	3.9 (1)
C(33A)*	10861 (16)	5093 (12)	1566 (16)	6.3 (3)
C(34A)*	9811 (12)	4460 (9)	816 (13)	4.9 (2)
C(35A)*	8877 (12)	4461 (10)	-627 (13)	6.1 (3)
C(33B)*	11398 (12)	5116 (10)	237 (13)	5.7 (2)
C(34B)*	11106 (14)	4805 (11)	1286 (15)	5.7 (3)
C(35B)*	9604 (15)	4792 (11)	1163 (15)	6.7 (3)

* The occupancy factor is 0.5.

Table 1.* The atomic scattering factors are taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Calculations were carried out on an IBM 4381-R24 computer at Ochanomizu University.

Molecular orbital calculations by the PM3 method were performed with *MOPAC*, Version 6.01 (Stewart, 1991) on a HITAC M-880H computer at the Computer Center of the University of Tokyo. The ¹H NMR spectra (270 MHz) were recorded in acetone-*d*₆ or CDCl₃ between 203 and 318 K on a JEOL JNM-GSX270 spectrometer.

Results and discussion

Fig. 1. shows the crystal structure of (Ia)-benzene solvate (1:0.5). The benzene molecule lies on the

* Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS0665). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

center of symmetry, but orientational disorder was observed. The benzene molecule has short intermolecular contacts with the 3-phenyl groups of two molecules of (Ia).

Fig. 2 shows the molecular structure of (Ia) with atom numbering. Selected bond distances and angles are summarized in Table 2. The (Ia) molecule is in a *meso* form, which adopts a *gauche* conformation in the crystal, and the molecular structure is closely related to that of (Ib). The C(3)—C(3') bond of (Ia) [1.596 (6) Å] is longer than the average value (1.588 Å) for hexa-substituted Csp^3-Csp^3 bonds (Allen *et al.*, 1987), but shorter than that of (Ib) [1.624 (4) Å]. The C(3)—C(11) and C(3')—C(11') distances are also longer than the average value for Csp^3 (quarternary)—C(aryl) bonds (1.527 Å). Kalyani, Manohar & Mani (1967) reported that biphtalidyls (IIa) and (IIb) exist in a centrosymmetric *anti* conformation in the crystal and that the C(3)—C(3') bond distance of (IIb) is 1.571 Å, which is much shorter than that of (Ia) or (Ib). In some molecules containing a Csp^3-Csp^3 bond with large repulsion between the vicinal substituents, *e.g.* *meso*-3,4-dicyclohexyl-2,2,5,5-tetramethylhexane, a highly

deformed *gauche* form dominates over the centrosymmetric *anti* form. The *anti* form is considered to be less stable since there is no effective way of releasing nonbonded repulsion across the central bond due to molecular symmetry (Beckhaus *et al.*, 1978). In the case of (Ia), deformation from a staggered conformation is not so large [Fig. 3(a)], but the corresponding bond angles around C(3) and C(3') are somewhat different, especially C(3)—C(3')—C(2') which is larger than C(2)—C(3)—C(3') by 4.7°. As for the other bond distances and angles, there is no significant difference between the two halves of (Ia).

Elongation of the C(3)—C(3') bond in (Ia) and (Ib) may be caused not only by nonbonded repulsions, but also by through-bond interactions between the two phenyl groups at C(3) and C(3') and/or the carbonyl groups at C(2) and C(2'). The torsional angles of C(3')—C(3)—C(11)—C(12) (-94.7°) and C(3)—C(3')—C(11')—C(12') (106.2°) are close to $\pm 90^\circ$, indicating that the orientation of the phenyl groups is favorable for through-bond interactions (Osawa & Kanematsu, 1986). Since torsional angles of C(3')—C(3)—C(2)—O(10) and C(3)—C(3')—C(2')—O(10') are -52.8 and 60.8° , respectively, contribution to the elongation of C(3)—C(3') of through-bond interactions between the carbonyl groups is considered to be small.

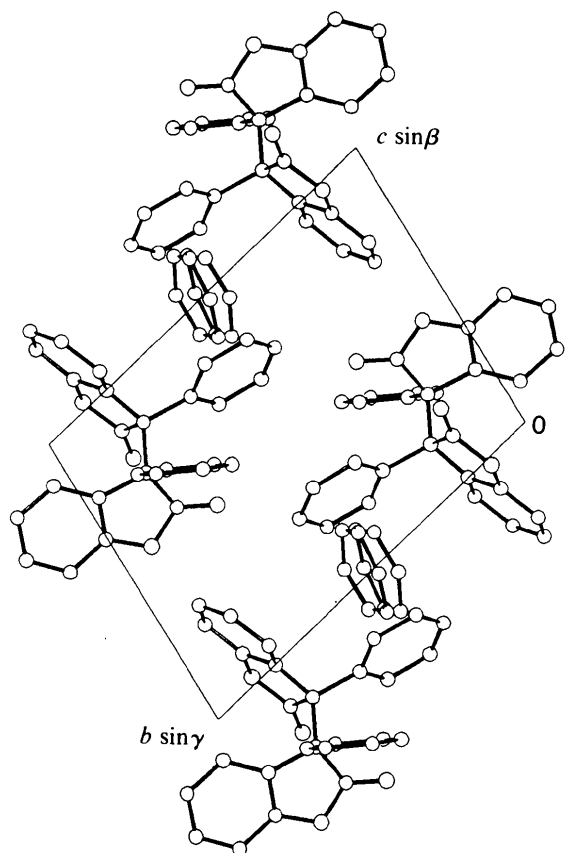


Fig. 1. Crystal structure of the benzene solvate of (Ia) viewed along the *a* axis.

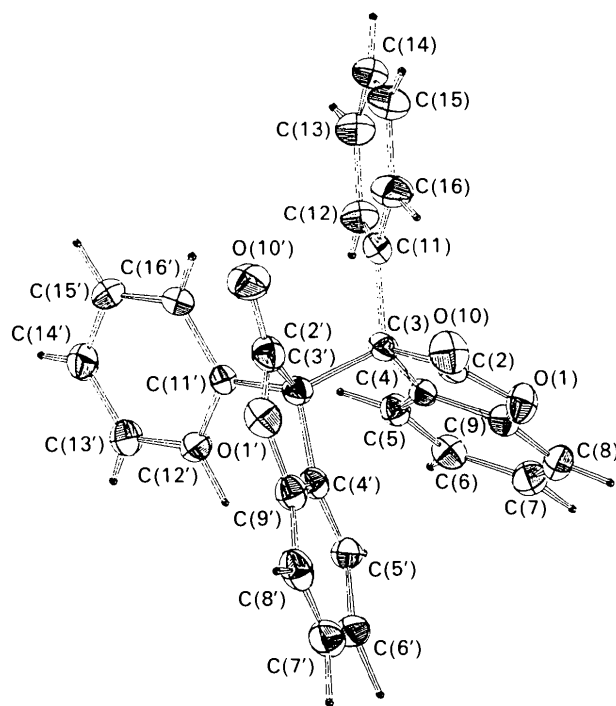


Fig. 2. ORTEP plot (Johnson, 1965) of (Ia) with the atom numbering. The anisotropic ellipsoids for non-H atoms represent 30% probability.

Table 2. Selected bond distances (Å) and angles (°)

O(1)—C(2)	1.369 (5)	O(1')—C(2')	1.380 (6)
O(1)—C(9)	1.385 (5)	O(1')—C(9')	1.381 (5)
C(2)—C(3)	1.549 (6)	C(2')—C(3')	1.533 (6)
C(2)—O(10)	1.178 (6)	C(2')—O(10')	1.913 (6)
C(3)—C(4)	1.506 (5)	C(3')—C(4')	1.526 (5)
C(3)—C(11)	1.553 (6)	C(3')—C(11')	1.544 (5)
C(3)—C(3')	1.596 (5)		
C(4)—C(5)	1.385 (6)	C(4')—C(5')	1.377 (6)
C(4)—C(9)	1.382 (6)	C(4')—C(9')	1.371 (6)
C(5)—C(6)	1.381 (6)	C(5')—C(6')	1.394 (7)
C(6)—C(7)	1.381 (6)	C(6')—C(7')	1.385 (8)
C(7)—C(8)	1.379 (7)	C(7')—C(8')	1.364 (8)
C(8)—C(9)	1.364 (6)	C(8')—C(9')	1.393 (7)
C(2)—O(1)—C(9)	108.9 (3)	C(2')—O(1')—C(9')	107.5 (3)
O(1)—C(2)—C(3)	109.6 (3)	O(1')—C(2')—C(3')	110.8 (4)
O(1)—C(2)—O(10)	121.3 (4)	O(1')—C(2')—O(10')	119.6 (4)
C(3)—C(2)—O(10)	129.2 (4)	C(3')—C(2')—O(10')	129.6 (4)
C(2)—C(3)—C(4)	100.4 (3)	C(2')—C(3')—C(4')	100.0 (3)
C(2)—C(3)—C(11)	108.7 (3)	C(2')—C(3')—C(11')	108.1 (3)
C(2)—C(3)—C(3')	106.6 (3)	C(3)—C(3')—C(2')	111.3 (3)
C(4)—C(3)—C(11)	111.5 (3)	C(4')—C(3')—C(11')	113.1 (3)
C(4)—C(3)—C(3')	112.9 (3)	C(3)—C(3')—C(4')	110.6 (3)
C(11)—C(3)—C(3')	115.4 (3)	C(3)—C(3')—C(11')	112.9 (3)
C(3)—C(4)—C(5)	133.9 (4)	C(3')—C(4')—C(5')	133.7 (4)
C(3)—C(4)—C(9)	108.5 (3)	C(3')—C(4')—C(9')	107.9 (3)
C(5)—C(4)—C(9)	117.6 (4)	C(5')—C(4')—C(9')	118.4 (4)
C(4)—C(5)—C(6)	119.8 (4)	C(4')—C(5')—C(6')	119.1 (4)
C(5)—C(6)—C(7)	120.7 (4)	C(5')—C(6')—C(7')	120.5 (5)
C(6)—C(7)—C(8)	120.5 (4)	C(6')—C(7')—C(8')	121.5 (5)
C(7)—C(8)—C(9)	117.6 (4)	C(7')—C(8')—C(9')	116.4 (5)
O(1)—C(9)—C(4)	112.0 (3)	O(1')—C(9')—C(4')	113.5 (4)
O(1)—C(9)—C(8)	124.0 (4)	O(1')—C(9')—C(8')	122.4 (4)
C(4)—C(9)—C(8)	123.9 (4)	C(4')—C(9')—C(8')	124.0 (4)

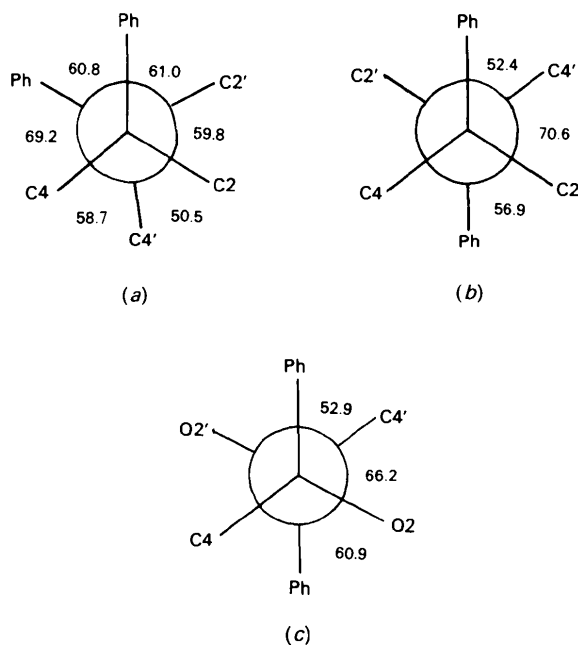


Fig. 3. Newman projections for C(3)—C(3') of (Ia) and (IIa). The figures show torsional angles (°). (a) The *gauche* form of (Ia) determined by X-ray methods; (b) the *anti* form of (Ia) optimized by the PM3 method; (c) the *anti* form of (IIa) optimized by the PM3 method.

In order to obtain further information on the structural features of (I) and (II), conformational analyses of (Ia), (Ib) and (IIa) were performed by the PM3 method (*MOPAC*). Table 3 summarizes the observed and calculated C(3)—C(3') bond distances and heat of formation (ΔH_f). From the calculation of ΔH_f , the higher value of (Ia) than that of (IIa) was considered to correspond to the observation that (Ia) suffered from more severe steric hindrance than (IIa). As for (Ia), the structure of the *anti* conformer was optimized with C_i symmetry as another local minimum. The optimized structure of *anti*-(Ia) is in a staggered conformation, which is similar to that of (IIa) [Figs. 3(b) and (c)]. The *anti* form of (Ia) was calculated to be slightly more stable than the *gauche* form. It seems that, however, (Ia) and (Ib) exist predominantly in the *gauche* conformation, not only in the crystal but also in solution (*vide infra*). Although geometry optimization was performed from the structure determined by X-ray methods, the C(3)—C(3') distances of (Ia) and (Ib) cannot be properly reproduced. According to the calculation, substitution by Cl at the 5- and 5'-positions has no effect on the C(3)—C(3') distance, while the observed C(3)—C(3') distance of (Ib) was longer than that of (Ia). This discrepancy between the calculated and observed bond distances may suggest that the C(3)—C(3') bonds in (Ia) and especially in (Ib) should be lengthened by some intramolecular force which is not considered in the calculation and/or intermolecular interaction. Although which factor contributes to the elongation of C(3)—C(3') in the crystal of (Ib) is unclear at the present stage of investigation, the weakness of the bond affords a plausible explanation for the fact that (Ib) dissociates into radicals by mechanical force more easily than (Ia) (Kubota, 1994).

The ^1H NMR spectra of (Ia) and (Ib) were informative with regard to the conformation of these molecules in solution. In the spectrum of (Ia) recorded in CDCl_3 at 293 K, a broad doublet signal was observed at δ 6.4, which is a little sharpened at 318 K. In the spectrum of (Ib) in acetone- d_6 , the corresponding signal appeared at δ 6.5 as a broad singlet. These signals were assigned to 4- and 4'-H [C(5)—H and C(5')—H in Fig. 1]. The signal at δ 6.5 in the spectrum of (Ib) split into two singlets at 233 K, but because of overlap with another signal the coalescence temperature could not be determined accurately. The temperature dependence of the ^1H NMR spectrum was also investigated for the *p*-chlorophenyl derivative (Ic) in the temperature range 203–295 K in acetone- d_6 . It was found that as the temperature decreased, a broad doublet at δ 6.5 further broadened and split into two signals at a temperature lower than the coalescence point (*ca* 263 K). Finally, sharp doublets were observed at δ

Table 3. Comparison of the C(3)—C(3') bond distance and heat of formation between bis(benzofuranonyl) and bisphthalidyl

Compound	Bond distance	PM3	ΔH_f (kcal mol ⁻¹)
	X-ray	(Å)	
(Ia) gauche	1.596 (5)	1.564	-14.50
(Ia) anti	—	1.574	-14.71
(Ib) gauche	1.624 (4)	1.564	—
(IIa) anti	—	1.586	-22.10
(IIb) anti	1.571	—	—

6.05 and 6.93 with an integration ratio of 1:1 at 203 K. At 263 K the exchange rate was 530 s⁻¹ and the free activation energy ΔG (263 K) was estimated to be 12 kcal mol⁻¹. If molecule (I) exists in the conformation observed in the crystal, C(5)—H, which is located above the 3'-phenyl group, is probably more shielded than C(5')—H. The observed dynamic process is probably due to the interconversion between (+)-gauche and (-)-gauche forms through restricted rotation around the C(3)—C(3') bond. No other signal assignable to 4- and 4'-H was observed, indicating that the population of the anti form was negligibly small.

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Structure and Thermal Motion of Tetrakis(trichlorophosphazeno)phosphonium Dichloroiodate(I), [P(NPCl₃)₄]⁺[ICl₂]⁻.2[(CCl₄)_x(CHCl₃)_{1-x}], $x = 0.67$ (2)

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Dedicated to Professor Dr Josef Schurz on the occasion of his 70th birthday

Abstract

[P(NPCl₃)₄]⁺[ICl₂]⁻.2[(CCl₄)_x(CHCl₃)_{1-x}], $x = 0.67$ (2), $M_r = 1119.1$, tetragonal, $I4_1/acd$, $a = 16.114$ (4), $c = 27.777$ (7) Å, $V = 7213$ (1) Å³, $Z = 8$, $D_x = 2.06$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 2.76$ mm⁻¹, $F(000) = 4251.5$, $T = 293$ K, $R = 0.0434$, $wR = 0.0452$ for 596 unique observed reflections and 80 parameters. The cation, anion and solvent molecules show site symmetries of S_4 , D_2 and C_2 , respectively. In the cation, the observed P—N distances of 1.452 (17) and 1.481 (17) Å are extremely short. Taking the observed P...P distance of 2.928 (4) Å as

a basis, a correlation of the P—N—P bond angles with the P...P distances found in the Cambridge Structural Database (CSD) suggests a P—N—P angle of *ca* 136° rather than the observed angle of 173.3 (11)°. The N and Cl atoms especially have unusually large displacement parameters. The thermal motion analysis shows that the 'rigid-bond' test is fulfilled. The PN₄ tetrahedron, the almost regular P(·P)₄ tetrahedron and the NPCl₃ tetrahedron appear to be rigid bodies; the [P(NPCl₃)₄]⁺ cation as a whole does not. Furthermore, the non-rigid body motion cannot be explained by allowance for intramolecular torsion. All these facts can only be