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FACTORS AFFECTING THE REVERSIBILITY OF THE ELECTROPHILIC STEP IN OLEFIN BROMINATION. THE CASE OF 5*H*-DIBENZO[*a*, *d*]CYCLOHEPTENE

GIUSEPPE BELLUCCI,* CINZIA CHIAPPE AND FRANCO MARIONI
Dipartimento di Chimica Bioorganica, Università di Pisa, Via Bonanno 33, 56100 Pisa, Italy
AND
FABIO MARCHETTI
Dipartimento di Chimica e Chimica Industriale, Universitá di Pisa, Via Risorgimento 33, 56100 Pisa, Italy

The tendency of ion-pair intermediates generated by treatment of *trans*-10-bromo-10,11-dihydro-11-hydroxy-5*H*-dibenzo[*a*, *d*]cycloheptene (5) with HBr to release Br_2 giving 5*H*-dibenzo[*a*, *d*]cycloheptene (1) has been evaluated. The observed 9 : 1 ratio between ion-pair collapse to the *trans*-dibromide (7) and Br_2 release to olefin 1, as compared with the 3 : 7 ratio found with the 5*H*-dibenz[*b*,*f*]azepine-5-carbonyl chloride system, has been interpreted as indicating a much lower propensity for reversibility of ion-pair formation in the bromination of 1. The structural parameters obtained by x-ray diffraction of the dibromide 7 show for this compound an angle strain at C-10 and C-11 analogous to that found in *trans*-10,11-dibromo-10,11-dihydro-5*H*-dibenz[*b*,*f*]azepine-5-carbonyl chloride. Olefin 1 adds Br_2 in 1,2-dichloroethane at 25 °C according to a third-order rate law, with $k_3 = 30(3)\ \mathrm{M}^{-2}\ \mathrm{s}^{-1}$. About 10% of 5-bromo-5*H*-dibenzo[*a*, *d*]cycloheptene, arising from collapse of a dibenzo[*a*, *d*]tropylium ion intermediate (9), is formed in this reaction besides the expected *trans*-dibromide 7. Spectral evidence for the formation of 9, arising by rearrangement of a first formed weakly bridged ionic intermediate in the reaction of 1 with Br_2, is presented. the results obtained with the 5*H*-dibenzo[*a*, *d*]cycloheptene system have been rationalized on the basis of the formation of very weakly bridged intermediates having a much lower tendency to revert back to olefin and Br_2 with respect to the corresponding symmetrically bridged bromonium ions.

INTRODUCTION

The electrophilic bromination of olefins, a classical example of multi-step organic reactions, has been subjected for many years to very extensive mechanistic and product investigations under a variety of conditions.[1] It is long-established that bridged or open bromo cations can be involved as the reaction intermediates.[2] Complete bromine bridging, and a positive charge borne only by the heteroatom, have been inferred[2] for both transition states and intermediates of the bromination of simple alkenes, although an asymmetric charge distribution is implied by regiochemical and spectroscopic results on bromonium ions derived from *gem*-disubstituted alkenes. A multi-pathway mechanism,[2] involving both bromonium and β-bromocarbonium ions formed by discrete pathways, and whose competition depends on the substituents on the aromatic rings has been proposed instead for the bromination of ary olefins, including stilbenes,[3] styrenes[4] and α methylstilbenes.[5] This interpretation has, however recently been questioned, because of the difficulty ‘t understand how two distinct intermediates, rather tha a unique ion whose charge would be distribute between the carbons and bromine atoms, coexist.’ Most studies carried out before the 1980s had bee interpreted as showing (or by assuming) that the ioni intermediates are formed irreversibly and that their collapse to the final dibromide products is a very fast process. Only in the last few years has it becom increasingly clear that the ion formation step ca actually be reversible,[6–12] and that a spectrum of situations ranging from exclusive ion reversal to progressively irreversible ion formation can be found depending on the relative heights of the product-forming barrier and of the reverse barrier.

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*Author for correspondence

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Although some factors involved in determining these barriers have been identified,[9-12] many gaps still remain in our knowledge of this phenomenon and of its repercussions in the structure–reactivity relationships for olefin bromination. As a contribution to the clarification of these points, we undertook an investigation aimed at seeking information about the structural effects on the reversibility of the formation of ion-pair intermediates during the electrophilic bromination of olefins in low-polarity aprotic solvents, by comparing the behaviour of 5*H*-dibenzo[*a*,*d*]cycloheptene (**1**) with that of the previously investigated 5*H*-dibenz[*b*,*f*]azepine-5-carbonyl chloride[9,12] and stilbene systems.[8] As already shown,[8,9] ion-pair intermediates of this type can be easily generated also by reacting the corresponding bromohydrin derivatives with gaseous hydrogen bromide. In this case, the possibility of release of Br_2 from the ion pair can be revealed by the formation of olefin, the HBr gas stream acting as a Br_2 scavenger and preventing its readdition. If the Br_2 removal is efficient enough, the ratio of the olefin formed to the dibromide arising from the normal collapse of the ion pair gives a rough evaluation of the tendency of the bromonium ions involved to revert back to Br_2 and olefin. The results have shown for the 5*H*-dibenzo[*a*, *d*]cycloheptene system a low tendency for ion reversion, which is related to the weakly bridged structure of the cationic intermediate formed both in the reaction of bromohydrin **5** with HBr and in the reaction of olefin **1** with Br_2.

RESULTS

Reaction of bromohydrin 5 with HBr

In order to prepare the required *trans*-10-bromo-10,11-dihydro-11-hydroxy-5*H*-dibenzo[*a*,*d*]cycloheptene (**5**), epoxide **2**[13] was treated with gaseous HBr in three low-polarity aprotic solvents, 1,2-dichloroethane, chloroform and carbon tetrachloride. The best results were obtained using a stoichiometric amount of HBr in the last solvent, from which bromohydrin **5** precipitated. A 30% yield of **5** was thus obtained. The *trans-gauche* relationship of bromine and hydroxyl groups in **5** was shown by the NMR spectrum in $CDCl_3$, exhibiting for the C-10 and C-11 protons an AB quartet with $J = 9{\cdot}2$ Hz, indicating antiperiplanar α protons. The CCl_4 mother liquors contained variable amounts of *trans*-10,11-dibromo-10,11-dihydro-5*H*-dibenzo[*a*,*d*] cycloheptene (**7**), produced by further reaction of bromohydrin **5** with HBr, a product of the seven-membered ring contraction of **2**, 9,10-dihydroanthracene-9-carboxaldehyde (**4**)[14] and small amounts of anthracene-9-carboxaldehyde and anthracene, formed by further transformations of **4**.[14] Increasing the HBr to epoxide ratio resulted in an increased dibromide formation, whereas the use of chloroform or 1,2-dichloroethane as the solvent led to mixtures consisting of dibromide **7** and larger amounts of ring-contracted products, with only traces of **5**. Bromohydrin **5** reacted very fast with HBr in carbon tetrachloride, being completely converted into a mixture of dibromide **7** and olefin **1** when a vigorous stream of HBr was bubbled through a 10^{-2} M solution in CCl_4 for 5 min. The same products were obtained, in addition to some unreacted **5**, when the reaction was stopped after 2–3 min or when HBr and argon were simultaneously bubbled through. The crude reaction mixtures were analysed by high-performance liquid chromatography (HPLC) after addition of an appropriate standard in order to determine the product yields. The results of typical runs are reported in Table 1.

The overall yields of the detected products and starting materials were always $\geqslant 90\%$ and the olefin to dibromide ratio was constantly *ca* 1 : 9, independent of the amount of the unreacted bromohydrin, indicating that both **1** and **7** were stable under the reaction conditions. This was confirmed by separate experiments with **1** and **7**, which were recovered in $\geqslant 90\%$ yield after treatment with HBr in CCl_4.

Table 1. Product yields from the reaction of *trans*-10-bromo-10,11-dihydro-11-hydroxy-5*H*-dibenzo[*a*,*d*]cycloheptene (**5**) with HBr in CCl_4

	Yield (%)		
Time (min)	**5**	**7**[a]	**1**[a]
2	45	40(89)	5(11)
3	25	58(89)	7(11)
5[b]	30	58(91)	6(9)
5[c]	—	85(91)	8(9)

[a] Figures in parentheses are the relative percentages of **7** and **1**.
[b] Reaction carried out by bubbling HBr and argon simultaneously.
[c] Average of six runs: the error of the relative percentages of **7** and **1** is ±1%.

Reaction of olefin 1 with Br_2

When solutions of **1** and Br_2 in 1,2-dichloroethane were mixed and the UV–visible spectrum was immediately registered, the typical absorption band of the halogen appeared to be modified. The new spectrum exhibited two small bands superimposed around the 410-nm maximum of Br_2, and absorptions slightly higher than those of Br_2 in the 450–600-nm range. The entire 350–600-nm spectrum decayed regularly with the progress of the bromination reaction and the solution became immediately transparent above 350 nm on addition of cyclohexene, an olefin that reacts very fast with Br_2.[15] In order to obtain a difference spectrum with respect to a solution of Br_2 alone, the reactivity of the **1**$-Br_2$ system was depressed by appropriately reducing the Br_2 concentration. The spectrum at 25 °C of a 1,2-dichloroethane solution containing $3{\cdot}6\times10^{-4}$ M Br_2 and $3{\cdot}6\times10^{-3}$ M **1**, registered immediately after mixing the reagents, that of Br_2 alone at the same concentration and the difference spectrum in the 350–600-nm range are shown in Figure 1 (an intense absorption of **1** prevents the difference spectrum below 350 nm from being attained). This difference spectrum, showing pairs of bands at 380 and 398 nm and at *ca* 510 and 540 nm, was identical with that reported for the dibenzo[*a*, *d*]tropylium ion.[16]

In agreement with the involvement of ionic species at detectable concentrations, a 5×10^{-3} M solution of **1** and Br_2 exhibited a low but definite conductivity, $\chi=2{\cdot}25$ μS cm^{-1}, compared with a value of $\chi=0{\cdot}13$ μS cm^{-1} found for solutions of Br_2 and *trans*-stilbene at the same concentrations. On the basis of the UV–visible spectrum, using the molar absorption coefficients reported for the dibenzo[*a*,*d*]tropylium ion in 98% H_2SO_4,[16] the concentration of this ion in the above solution immediately after mixing the reagents could be roughly evaluated to be *ca* 10^{-5} M.

The rate of consumption of Br_2 was measured both at 1 : 1 ratio of the two reagents and with a large excess of **1**, monitoring at 410 nm, where the absorption of the dibenzo[*a*,*d*]tropylium ion was negligible (see Figure 1). (A contribution to the 410-nm absorbance could arise from the Br_3^- counteranion of **9**, having a molar absorptivity 2·5 times as large as that of Br_2 at this wavelength. However, owing to the very low concentration of this species, its contribution can be neglected.) The reaction was found to follow cleanly for at least two half-lives the third-order rate law of equation (1), usually observed for olefin bromination in 1,2-dichloroethane,[8,9,17,18] with $k_3=30(3)$ M^{-2} s^{-1} at 25 °C.

$$-\mathrm{d}[Br_2]/\mathrm{d}t=k_3[\mathrm{Ol}][Br_2]^2 \qquad (1)$$

The product formation was monitored by HPLC

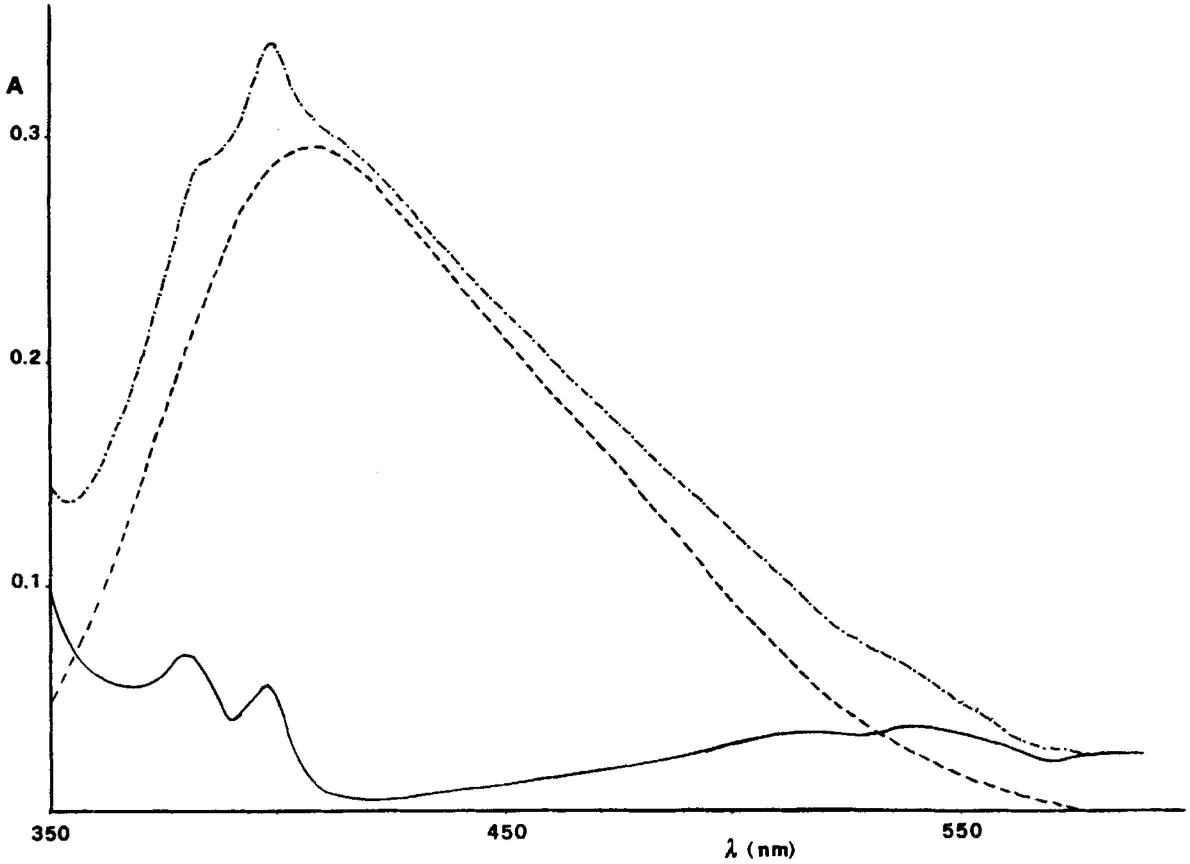


Figure 1. UV–visible spectra in 1,2-dichloroethane at 25 °C of $3{\cdot}6\times10^{-4}$ M Br_2(----), $3{\cdot}6\times10^{-4}$ M Br_2 and $3{\cdot}6\times10^{-3}$ M 5*H*-dibenzo[*a*,*d*]cycloheptene (**1**) (— · —) and their difference (———)

during the course of the bromination reaction. Only dibromide **7** and small amounts of a second product, identified as 5-bromo-5*H*-dibenzo[*a*,*d*]cycloheptene (**10**) as discussed below, were detected in addition to unreacted **1**. At 90% conversion the ratio of the monobromo derivative **10** to the dibromo derivative **7** was 1:8.

The pure dibromide **7** was isolated from a preparative run in 80% yield by crystallization from acetonitrile. The *trans* orientation of the C-10 and C-11 substituents was shown by the equivalence of both the α protons and the methylene protons in the NMR spectrum. The latter protons are expected to be non-equivalent in *cis*-10,11-disubstituted 10,11,-dihydro-5*H*-dibenzo[*a*,*d*] cycloheptene derivatives (see, for instance, *cis*-10,11-dihydro-10,11-dihydroxy-5*H*- dibenzo[*a*,*d*]cycloheptene[19]). An approximately antiperiplanar arrangement of the two bromine atoms was further established by the x-ray diffractometric study reported below.

The minor bromination product was identified as 5-bromo-5*H*-dibenzo[*a*,*d*]cycloheptene (**10**) by comparison of its HPLC retention time and UV–visible spectrum with those of the product obtained by reaction of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol with gaseous HBr in diethyl ether. Structure **10** was confirmed by the NMR spectrum, showing two singlets, due to one proton α to bromine and to two olefin protons.

As previously found with the structurally related 5*H*-dibenz[*b*,*f*]azepine-5-carbonyl chloride[9] and with 5*H*-dibenz[*b*,*f*]azepine-5-carboxamide,[20] olefin **1** did not react with tetrabutylammonium tribromide in 1,2-dichloroethane, in contrast to most other olefins.[21]

Colourless crystals of dibromide **7** first turned bright black and the yellow on prolonged standing even at −20 °C. However, the NMR spectrum of the dissolved material showed no substantial modification. The more sensitive HPLC technique showed that a sample of the black product consisted of 95% unchanged dibromide and small amounts (2–3% each) of olefin **1** and of a compound having the retention time of a product of HBr elimination from **7**, presumably 10-bromo-5*H*-dibenzo[*a*,*d*]cycloheptene. The yellow material contained 92% dibromide **7**, again accompanied by small amounts (*ca* 3% each) of **1** and of the above-mentioned elimination product. In addition, small amounts of two products, whose UV-visible spectra showed intense absorptions around 250 and 260 nm and a series of peaks between 340 and 410 nm, pointing to brominated anthracene derivatives, were also present in the yellow material and were responsible for the colour. One of these products had the HPLC retention time of 9,10-dibromoanthracene, obtained by reaction of anthracene with Br_2.[22] The fact that the overall amounts of all these by-products were always low indicated that the observed colour changes were actually due to surface

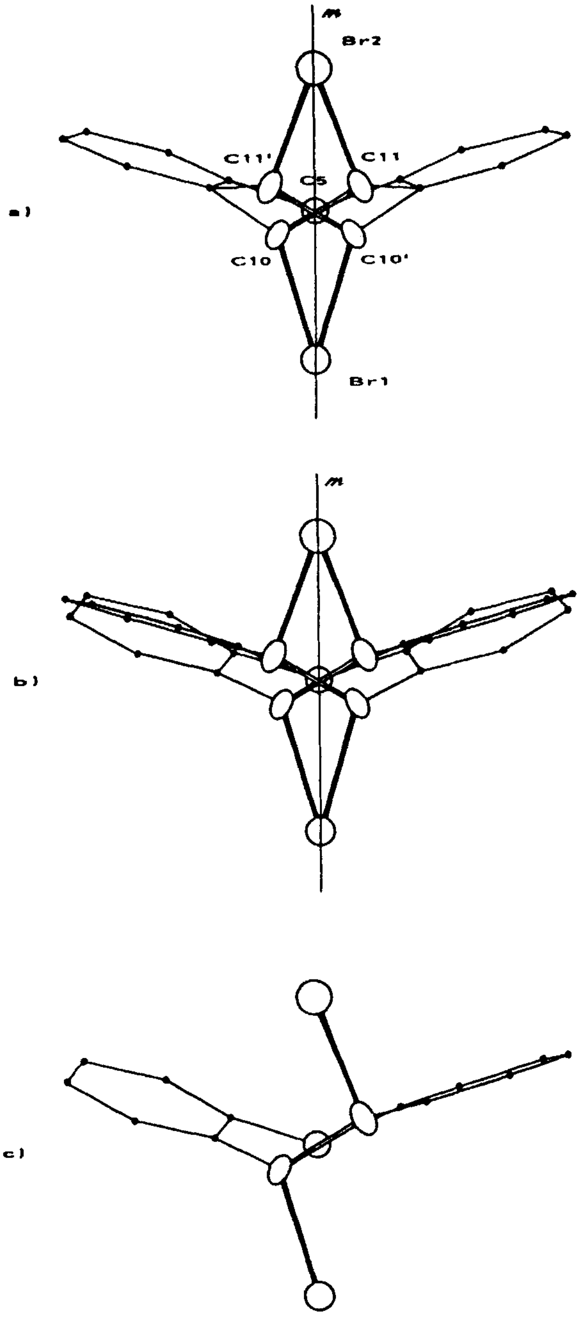


Figure 2. View of the molecular structure of dibromide **7** projected on a plane normal to the direction obtained connecting the C-5 atom and the centre of the X-like pattern of C-10 and C-11: (a) before the introduction of the two different conformations; (b) the final result after refining with the two superimposing conformations; (c) final aspect of one conformation

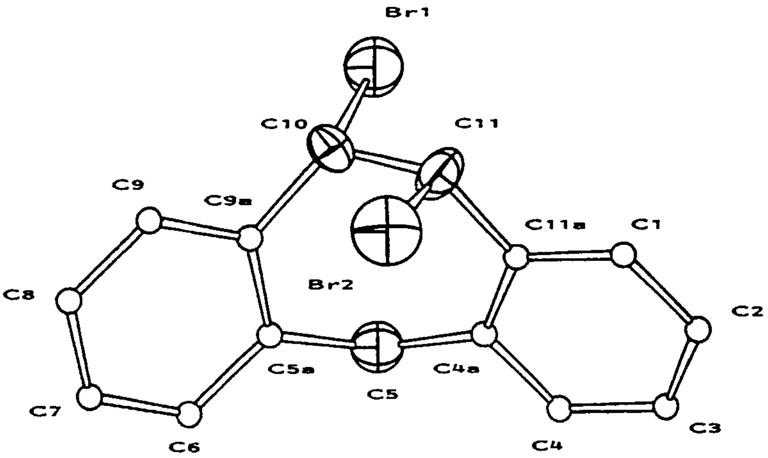


Figure 3. ORTEP projection of the molecular structure of dibromide 7 in the direction of minimum superimposition, with the numbering scheme. For the atoms refined with anisotropic thermal factors, ellipsoids are represented at 50% probability

phenomena, the bulk of the product remaining unchanged.

X-ray structure of dibromide 7

Crystals of the *Cmc*2₁ space group were found to contain molecules of dibromide 7 statistically distributed in two different conformations with the bromine atoms and the methylene carbon perfectly superimposed (Figure 2). A perspective view of the molecular structure in the direction of minimum superimposition is shown in Figure 3. Final atomic coordinates and isotropic thermal parameters with standard deviations are listed in Table 2. Table 3 contains bond distances and angles, excluding those relative to the phenyl rings, to which an ideal hexagonal geometry was imposed in the refinement (see experimental). The Br(1)—C(10)—C(11)—Br(2) torsion angle is 171(1)°. Similar values have been observed in *trans*-10,11-dibromo-10,11-dihydro-5*H*-dibenzo [*b*, *f*] azepine-5-carbonyl chloride (**15**, 162·4°)[9] and in *trans*-10,11-dibromo-10,11-dihydro - 5*H* - dibenz [*b*, *f*] azepine - 5 - carboxamide

Table 2. Atomic coordinates of non-hydrogen atoms in $C_{15}H_{12}Br_2$[a]

Atom	*x*/*a*	*y*/*b*	*z*/*c*	*B* or B_{eq}[b] (Å^2)
1-Br	1/2	0·4136(1)	0·36000	5·04(5)
2-Br	1/2	0·2284(1)	−0·1669(4)	5·19(5)
C-1	0·2952(9)	0·2065(12)	0·0808(14)	3·5(4)
C-2	0·2309(9)	0·1279(12)	0·1443(14)	3·5(4)
C-3	0·2569(9)	0·0497(12)	0·2716(14)	4·2(5)
C-4	0·3471(9)	0·0501(14)	0·3353(14)	4·1(6)
C-4a	0·4114(9)	0·1287(12)	0·2718(14)	5(1)
C-11a	0·3854(9)	0·2068(12)	0·1445(14)	2·5(3)
C-5	1/2	0·1202(11)	0·3774(19)	3·5(4)
C-6	0·6621(11)	0·0492(11)	0·2964(22)	3·4(4)
C-7	0·7487(11)	0·0673(11)	0·2217(22)	3·2(4)
C-8	0·7661(11)	0·1682(11)	0·1308(22)	4·0(5)
C-9	0·6971(11)	0·2509(11)	0·1145(22)	4·5(5)
C-9a	0·6105(11)	0·2327(11)	0·1892(22)	3·3(4)
C-5a	0·5931(11)	0·1319(11)	0·2801(22)	1(1)
C-10	0·5409(16)	0·3232(17)	0·1487(36)	3·7(5)
C-11	0·4498(17)	0·2932(20)	0·0629(30)	3·6(6)

[a] Estimated standard deviations given in parentheses refer to the last significant digits.
[b] B_{eq}, corresponding to one-third of the trace of the orthogonalized B_{ij} tensor, has been reported for 1-Br, 2-Br, C-5, C-10 and C-11, which have been refined with anisotropic thermal factors.

Table 3. Relevant structural parameters for *trans*-10,11-dibromo-10,11-dihydro-5*H*dibenzo[*a*,*d*]cycloheptene (7)[a]

Distances (Å)		Angles(°)	
Br(1)—C(10)	2·03(3)	Br(1)—C(10)—C(11)	103(2)
C(9a)—C(10)	1·49(3)	Br(1)—C(10)—C(9a)	113(2)
C(9a)—C(5a)	1·39(2)	C(9a)—C(10)—C(11)	121(2)
C(10)—C(11)	1·52(3)	C(5a)—C(9a)—C(10)	126(2)
		C(5)—C(5a)—C(9a)	118(1)
		C(4a)—C(5)—C(5a)	117·7(8)
Br(2)—C(11)	2·07(2)	Br(2)—C(11)—C(10)	99(2)
C(11a)—C(11)	1·51(3)	Br(2)—C(11)—C(11a)	109(1)
C(4a)—C(11a)	1·39(2)	C(11a)—C(11)—C(10)	120(2)
		C(4a)—C(11a)—C(11)	124(1)
		C(11a)—C(4a)—C(5)	130(1)

[a] Estimated standard deviations given in parentheses refer to the last significant digits.

(168°),[23] and appear to be typical of these tricyclic compounds. The C—C bond lengths are in agreement with the accepted values, and the two C—Br bonds are equivalent and fall at the upper limit of the normal sp^3 C—Br bond length range of 1·93–2·03 Å.[24] The C(9a)—C(10)—C(11) and C(11a)—C(11)—C(10) angles of 121(2) and 120(2)°, respectively, are instead considerably larger than the tetrahedral value, suggesting a high sp^2 character at both C-10 and C-11. Further, the C(11a)—C(4a)—C(5) angle also has an unusually large value of 130(1)°, as compared with the 118(1)° value for the corresponding C(5)—C(5a)—C(9a) angle. The two benzene rings form dihedral angles of 8·2(4) and 30·1(5)° with the average plane of the central seven-membered ring. The C-4a, C-5, C-5a, C-9a, C-10, C-11 and C-11a atoms are apart from this mean plane by 0·052, −0·308, 0·320, −0·065, −0·553, −0·006 and 0·100 Å, respectively, showing maximum puckering at C-10.

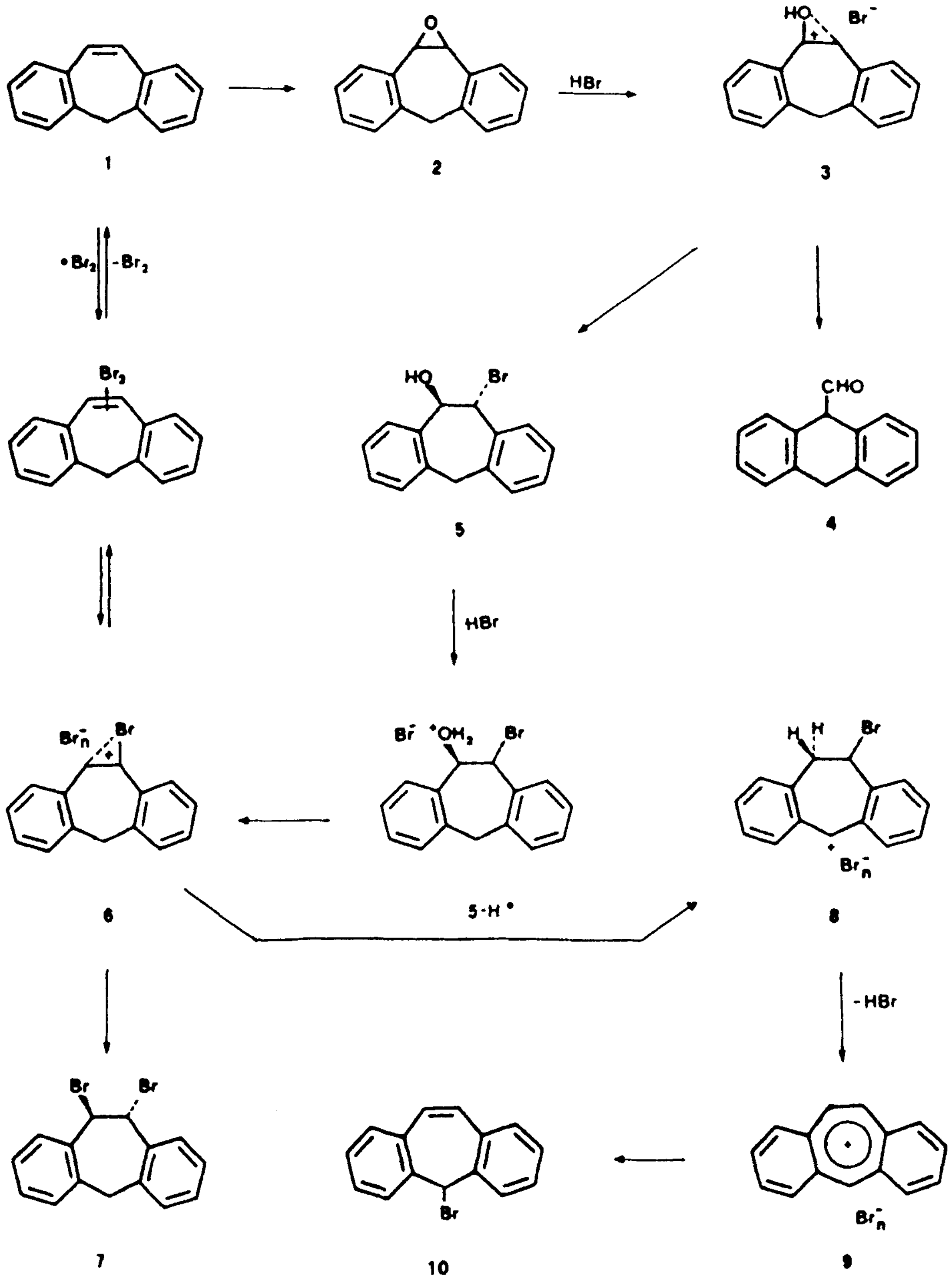
DISCUSSION

The course of the reaction of bromohydrin **5** with HBr and that of olefin **1** with Br_2 can be represented as shown in Scheme 1, where Br_n^- is Br^- when the ion pairs are generated from **5** and HBr and is Br_3^- when they are produced in the bromination of **1**. Scheme 1 also shows the course of the reaction of epoxide **2** with HBr.

The formation of large amounts of aldehyde **4** at the expenses of the normal oxirane ring opening product **5** in the last reaction is consistent with an extensive involvement of ions of type **3**, with a high localization of positive charge at a benzylic carbon (or of an open β-hydroxycarbonium ion),[14] which undergo more easily a seven-membered ring contraction than attack by Br^-. The same rearrangement was observed in the reaction of **2** with $HClO_4$ in tetrahydrofuran–water,[14] and in the acid-catalysed ring opening of nitrogen-unsubstituted, alkyl-substituted[25,26] or $CONH_2$-substituted[27] 1a,10b-dihydro-6*H*-dibenz[*b*,*f*]oxireno[*d*]azepine derivatives, but not of the COCl-substituted derivative **12**,[9] in which the electron-withdrawing substituent hampers the development of a positive charge at the oxirane carbons.

An ionic intermediate of type **6**, bearing most of the positive charge on a benzylic carbon with only a very weak bromine bridging, is likewise expected to be formed both in the reaction of bromohydrin **5** with HBr and in that of olefin **1** with Br_2. (A multi-pathway scheme (see Ref. 2) involving both a bromonium and a β-bromocarbonium ion intermediate, with a predominant contribution of the latter, could also explain the present results. In our opinion, in the present case a distinction between these two alternative formulations can only be speculative.) The *trans*-dibromide **7** is then formed by attack of the counteranion at the carbon of the cation, whereas attack at bromine leads to olefin **1**, probably through an olefin–Br_2 charge-transfer complex of the type involved in olefin bromination.[17] {The formation of *trans*-dibromide, without any *cis* isomer, has been observed also in the bromination of 5*H*-dibenz[*b*,*f*]azepine derivatives, irrespective of the presence of substituents at N-5 able to allow stabilization ($CONH_2$, see Ref. 23) or destabilization (COCl, see Ref. 9) of a carbonium ion centre at C-10 or C-11, and seems therefore to be typical of these tricyclic systems.}

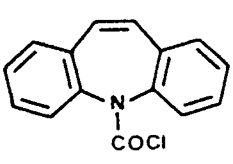
An alternative reaction pathway of **6** may consist in a hydride shift from C-5 to C-10 to give species **8**, which can lose HBr leading to the more stable dibenzo[*a*,*b*]tropylium ion **9**, a reaction reminiscent of the tropylium bromide formation from cycloheptatriene and Br_2.[28] Unequivocal spectral evidence for the formation of species **9** has actually been obtained in the reaction


1
2
3
HBr
HO
Br⁻
+Br₂
-Br₂
Br₂
HO
Br
CHO
5
4
HBr
Br⁻ₙ
Br
Br⁻
⁺OH₂
H
Br
Br⁻ₙ
6
8
5-H⁺
-HBr
Br
Br
Br
Br⁻ₙ
7
10
9

Scheme 1

of **1** with Br_2. (The electronic spectrum of the dibenzo[*a,d*]tropylium ion is a very typical one. Ions of the diphenylmethyl type such as **8** have very different spectra.[29]) The formation of about 10% of the 5-bromo derivative **10**, in addition to *trans* addition product **7**, in the latter reaction can be rationalized by a collapse of **9** at C-5. (Collapse of **9** at C-10 or C-11 is probably disfavoured by the loss of the aromatic character of one of the phenyl rings in the product). It can be observed that the accumulation of **9** at a concentration sufficient for its detection during the bromination of **1** is probably due to the presence of an excess of Br_2, maintaining the counteranion in the more stable, less nucleophilic Br_3^- form. [The association constant of Br^- and Br_2 to Br_3^- in 1,2-dichloroethane at 25 °C is $\geqslant 2 \times 10^7$ M^{-1} (see Ref. 18]. In fact, when the excess of halogen was rapidly removed by addition of a reactive olefin, the dibenzo[*a,d*]tropylium absorptions immediately disappeared as a consequence of a fast attack of the anion in the Br^- form at C-5 to give product **10**. The formation of this product in the reaction of **1** with Br_2 but not in that of **5** with HBr is attributable to the different lifetimes of the intermediates of type **6** formed in the two reactions. (No 5*H*-dibenzo[*a,d*]cyclohepten-5-ol, which could have been formed by hydrolysis of **10** during the work-up, was even detected by HPLC). This may be due both to the different solvent and to the different nature of the counteranion that is formed as Br_3^- in the bromination of **1** (as shown by the second-order dependence on [Br_2] of the bromination rate)[18,19] and as Br^- in the HBr reaction of **5**. A faster rate of direct collapse of ion pair **6** is expected to prevent rearrangement to **8** and **9** in the latter case.

The 9 : 1 value of the ratio of **7** to **1** found in all runs reported in Table 1, irrespective of the reagent conversion and of the flow of gas bubbled through during the reaction, strongly indicates that in the 5*H*-dibenzo[*a,d*]cycloheptene system the rate of the reverse process leading from ion pair **6** to olefin **1** and Br_2, although not negligible, is much lower than that of collapse of **6** to the *trans*-dibromide **7**. This is at variance with the results previously obtained with 10-bromo-10,11-dihydro-11-hydroxy-5*H*-dibenz[*b,f*]azepine-5-carbonyl chloride (**13**), where the ratio between collapse to dibromide **14** and loss of Br_2 to give olefin **11** was *ca* 3 : 7 in carbon tetrachloride.[9] Further, the presently observed ratio for **7** to **1** is also higher than the lowest limiting evaluation for the occurrence of ion-pair reversion to olefin and Br_2 in the stilbene system.[8]



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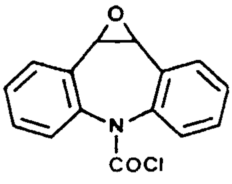
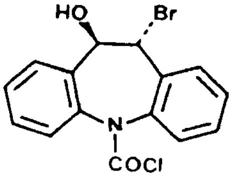
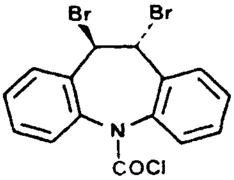


12



13



14

In principle, at least two reasons could account for these differences. First, the angle strain present in *trans*-10,11-dibromo-10,11-dihydro-5*H*-dibenz[*b,f*]azepine-5-carbonyl chloride (**14**), which had been considered to be responsible for the particularly high tendency of the corresponding bromonium–bromide ion pair to revert back to olefin **11** and Br_2,[9] could be lacking in dibromide **7**. Second, the extent of bridging of the intermediates could affect the propensity for reversibility.

The former hypothesis is ruled out by the structural parameters obtained by x-ray diffraction of **7**. These show that an angle strain of the type found in the dibenz[*b,f*]azepine dibromide **14** is present even around C-10 and C-11 of dibromide **7**, in which only two angles, Br(1)—C(10)—C(9a) and Br(2)—C(11)—C(11a), have normal sp^3 values, whereas two, C(9)—C(10)—C(11) and C(11a)—C(11)—C(10), are larger and the remaining two, Br(1)—C(10)—C(11) and Br(2)—C(11)—C(10), are smaller. These similar structural features, tending to favour the reversion from the intermediates to the reagents, should affect in a similar way the rates of the reverse reaction in the two tricyclic systems, if similar intermediates were involved. Thus, the observed large differences in reversibility give support to different intermediates.

Both the bromination of 5*H*-dibenz[*b,f*]azepine-5-carbonyl chloride (**11**) and the reaction of its *trans*-10,11-bromohydrin **13** with HBr had been assumed to occur through symmetrically bridged bromonium ions, the presence of the electron-withdrawing carbonyl chloride group on nitrogen preventing the localization of a positive charge at a benzylic carbon.[9] The situation is different in the case of the 5*H*-dibenzo[*a,d*]cycloheptene system, where the methylene bridge between two *ortho* positions of the phenyl rings may instead help, by electron release, charge development at either of the benzylic carbons and the intermediate is probably a very weakly bridged ion.

Both bromocarbonium and bromonium ion intermediates have been inferred for the bromination of *cis*-stilbene, differing from **1** only in the lack of the methylene bridge closing the seven-membered ring.[3c,30] In terms of a unique, more or less bridged intermediate, this corresponds to a bridging stronger than in **6** but much lower than in the bromonium ion arising from **11**. Hence the different propensities for reversibility observed for the 5*H*-dibenzo[*a*,*d*]cycloheptene, 5*H*-dibenz[*b*,*f*]azepine-5-carbonyl chloride and stilbene systems may be accounted for if strongly bridged bromonium ions are much more inclined to revert back to olefin and Br_2 than are weakly bridged or open ions. This is not unreasonable, since the barrier for the product-forming step would be expected to be higher in the case of a bridged ion, where nucleophilic attack by the counteranion at carbon requires a simultaneous breaking of one of the bromonium C—Br bonds, than for an open bromocarbonium ion, involving an easier collapse of the anion at the carbonium ion centre.

Work is in progress in order to check the general validity of the present results and to obtain further information concerning the influence of the positive charge distribution in the intermediates on the reversibility of the electrophilic step in olefin bromination.

EXPERIMENTAL

Melting points were determined on a Kofler block and are uncorrected. The ^{1}H NMR spectra were taken on a Bruker AC 200 instrument in $CDCl_3$ with TMS as internal reference. UV–visible spectra and kinetic measurements were obtained with a Varian Cary 2200 instrument. Conductivities were measured at 25 ± 0·05 °C with a Philips PW 9509 digital conductivity meter. HPLC analysis of all reaction mixtures was carried out with a Waters Model 600 E apparatus equipped with a Model 990 photodiode-array detector and a LiChrosorb C_{18} glass cartridge using methanol–water (75:25) as eluent at a flow-rate of 1 ml min^{-1}. In order to determine the yields, a carbon tetrachloride stock solution of 1-phenyl-1,2-dibromopropane, obtained by bromination of *trans*-1-phenylpropene with tetrabutylammonium tribromide, was added as an internal standard before the analysis. Commercial 1,2-dichloroethane (Carlo Erba, RPE grade, >99·5%) was treated as reported previously.[15] Bromine was withdrawn from 1-ml sealed vials (Carlo Erba, RPE grade, >99·5%) opened immediately before use.

trans-*10-Bromo-10-11-dihydro-11-hydroxy-5*H-*dibenzo*[a,d] *cycloheptene* (**5**). A 1 M solution of expoxide **2**[13] in carbon tetrachloride (1 ml) was added to 4 ml of a 0·25 M HBr solution in the same solvent and left for 1 h at room temperature, during which a crystalline product precipitated. The residual HBr was removed by bubbling argon through the reaction mixture and the solid, consisting of bromohydrin **5**, was collected by filtration, m.p. 103–105 °C. ^{1}H NMR δ 3·69 (d, 1H, CH_2, $J = 14·7$ Hz), 4·48 (d, 1H, CH_2, $J = 14·7$ Hz), 5·54 (d, 1H, CHBr, $J = 9·2$ Hz), 5·72 (d, 1H, *CH*OH, $J = 9·2$ Hz), 7·15–7·40 (m, 8H, aromatic protons). Attempts to crystallize this product led to decomposition. The product also decomposed on standing at room temperature, but could be stored at −20 °C.

HPLC analysis of the mother liquors revealed the presence of aldehyde **4**, identified by comparison of its retention time and UV spectrum with those of a sample obtained by $BF_3 \cdot Et_2O$-promoted rearrangement of **2**,[14] in addition to minor amounts of dibromide **7**, and trace amounts of anthracene-9-carboxaldehyde and anthracene, identified by comparison with authentic commercial samples.

Reactions of 5 with HBr. Gaseous HBr was bubbled into a 10^{-2} M solution of **5** (10 ml) in carbon tetrachloride at room temperature for the periods reported in Table 1. The reaction mixtures, washed with water and dried ($MgSO_4$), were analyzed by HPLC. The product yields are reported in Table 1.

Olefin **1** and dibromide **7** were found in ⩾90% yields by HPLC after bubbling HBr into carbon tetrachloride solutions of each for 5 min.

trans-*10,11-Dibromo-10,11-dihydro-5*H-*dibenzo* [a,d] *cycloheptene* (**7**). 1,2-Dichloroethane solutions of Br_2 (2·5 mmol) and **1** (2 mmol) were mixed (total volume 30 ml) and left for 3 h at room temperature in the dark. The resulting solution was then washed with saturated $NaHSO_3$ and water, dried ($MgSO_4$) and evaporated *in vacuo*. The residue was crystallized from acetonitrile to give 0·56 g of pure (HPLC) dibromide **7**, m.p. 150–160 °C, with gas evolution (lit.[31] m.p., 155–163 °C with gas evolution). ^{1}H, NMR, δ 4·54 (s, 2H, CH_2), 5·85 (s, 2H, CHBr), 7·20–7·38 (m, 8H, aromatic protons). Analysis: calculated for $C_{15}H_{12}Br_2$, C 51·17, H 3·43; found, C 50·8, H 3·25%.

*5-Bromo-5*H-*dibenzo*[a,d] *cycloheptene (10).* Gaseous HBr was bubbled into a solution of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol[17] (0·1 g) in diethyl ether (20 ml) for 5 min. Evaporation of the solution *in vacuo* gave a solid residue, which was crystallized from carbon tetrachloride to give pure **10** (0·09 g), m.p. 118–120 °C. ^{1}H HMR, δ 6·51 (s, 1H, CHBr), 7·17 (s, 2H, =CH—), 7·30–7·50 (m, 8H, aromatic protons). Analysis: calculated for $C_{15}H_{11}Br$, C 66·44, H 4·09; found, C 66·08, H 3·98%.

Spectrophotometric and kinetic measurements. Bromine solutions in 1,2-dichloroethane were prepared shortly before use and the concentrations adjusted to twice the desired initial ones. These solutions were thermostated at 25 °C, rapidly mixed with equal volumes of pre-thermostated solutions of **1** in the same solvent and the UV–visible spectrum, and also that of a solution of Br_2 alone of the same concentration, was registered in the 340–600nm range. This spectrum was periodically registered during the reaction. The decay of the Br_2 absorption was continuously followed at 410 nm under both pseudo-second-order conditions (3×10^{-2}–7×10^{-2} M **1** and 1×10^{-3}–2×10^{-3} M Br_2) and third-order conditions (4×10^{-3}–12×10^{-3} M **1** and Br_2) up to about 80% conversion. The absorbance–time data were fitted to the appropriate pseudo-second-order[15] or third-order integrated rate equations[8] and the rate constants obtained with the usual linear least-squares procedure. The k_3 value given in the text is the average of six independent measurements, the error being given as the standard deviation obtained from the deviations of individual measurements from the average values.

Product distribution during bromination. A 5×10^{-13} M 1,2-dichloroethane solution of **1** and Br_2 thermostated at 25 °C was divided into two parts. One part was used to follow the reaction spectrophotometrically in the 340–600-nm range. When the Br_2 absorbance at 410 nm was reduced to half, a sample was withdrawn from the second part of the solution and cyclohexene was added to remove the unreacted Br_2. HPLC analysis of this sample showed that the amount of **1** was also exactly reduced to half, the remainder having been converted to dibromide **7** accompanied by a small amount of monobromo derivative **10**. When the Br_2 absorption was reduced to 10%, HPLC analysis showed the presence of 10% of unreacted **1**, 80% of **7** and 10% of **10**.

Crystal structure analysis of dibromide **7**. Prismatic colourless crystals of dibromide **7** were mounted within Lindemann capillaries and were studied by the Weissemberg technique. The photographs showed orthorhombic symmetry; systematic absences suggested $Cmc2_1$ (n. 36) or $Cmcm$ (n. 65) as possible space groups.[35] The crystal showing the sharpest spots was used for intensity data collection, following the experimental conditions summarized in Table 4.

The collected intensities were corrected for Lorentz and polarization effects, whereas the absorption correction was applied in the refinement stage by using a semiempirical method.[32] The correct solution was found in the $Cmc2_1$ space group. Automatic direct methods[33] gave the position of the bromine atoms, both located on the symmetry plane at $x = 1/2$. A Fourier synthesis (phases of the structure factors obtained from the positions of the bromine atoms) showed a number of carbon atoms. The molecule was completed by alternating cycles of structure refinement with Fourier synthesis. However, the structure obtained at this stage presented a very distorted geometry: the plane *m* contained the bromine atoms and C-5; the two phenyl groups were plane related; the C-10 and C-11 atoms, connected to the bromine, were duplicated by the action of the plane, making an X-like pattern as shown in Figure 2. We have interpreted this result as being due to a statistical distribution of molecules of **7** in two different conformations with common 1-Br, 2-Br and C-5 atoms and the others slightly shifted. The

Table 4. Experimental data for the crystallographic analysis of *trans*-10,11-dibromo-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (**7**)[a]

Parameter		Value	Parameter	Value
Formula		$C_{15}H_{12}Br_2$	Scan width (°)	1·20
M		352·1	θ range (°)	3–25
Space group		$Cmc2_1$	h range	0–19
a (Å)		14·463(3)	k range	0–15
b (Å)		11·678(3)	l range	0–9
c (Å)		7·743(2)	Standard reflection	1 3 1
U (Å^3)		1307·8(6)	Intensity variation	$< \pm 3\sigma(\mathrm{Isr})$[b]
Z		4	Scan mode	$\theta/2\theta$
D_c (Mg m^{-3})		1·788	Condition for observed reflections	$I > 3\sigma(I)$
Reflections for lattice parameters	Number	26	No. of collected reflections	921
	θ range (°)	11–14	No. of reflections used in the refinement	606
Radiation		Mo Kα_1	Anisotropic least-squares on F	Full matrix
λ (Å)		0·70930	Max. least-squares shift-to-error ratio	0·23
$F(000)$		688	Min., Max. height in final Fourier map, ρ(eÅ^{-3})	−0·77, 0·46
T (K)		294	No. of refined parameters	70
Crystal size (mm)		0·20 × 0·13 × 0·73	$R = \Sigma \lvert \Delta F \rvert / \Sigma \lvert F_0 \rvert$	0·0489
Diffractometer		Ital Structures	$R' = [\Sigma w(\Delta F)^2 / \Sigma w F_0^2]^{1/2}$	0·0500
μ (mm^{-1})		61·13	$S = [\Sigma w(\Delta F)^2/(N - P)]^{1/2}$[c]	3·114
Absorption corrections (min., max.)		0·53–1·30	$k,\ g\{w = k/[\sigma^2(F_0) + gF_0{}^2]\}$	2·93, $1·24 \times 10^{-4}$
Slowest scan speed (° s^{-1})		0·033		

[a] Estimated standard deviations given in parentheses refer to the last significant digits.
[b] Isr is the mean of the intensities measured on the standard reflection.
[c] P = number of parameters, N = number of observations.

single conformation does not present a mirror plane; the *m* element results from the averaging of both conformations in the crystal. In order to verify this hypothesis we tried to refine the two limit conformations with an occupancy factor of 0·5, the same used for the atoms 1-Br, 2-Br and C-5, which lie in special position at $x = 1/2$. The program used for calculations[34] permitted the use of anisotropic thermal factors for 1-Br, 2-Br, C-10 and C-11, and a fixed geometry with isotropic thermal factors for the atoms of the phenyl groups. The model was successfully refined to a reliability factor of 0·059. [We have also considered the possibility that the actual Laue class is $2/m$ with $\beta = 90°$, and the mirror *m* normal to the α axis is not an operation of the space group (in this case *Cc*), but a twinning plane. On the basis of this model we carried out the refinement (no geometrical constraints, anisotropic thermal parameters for all the atoms) which resulted, notwithstanding the larger number of variable parameters, in a worse *R* value and a more distorted molecular geometry.]

A number of hydrogen atoms were located by difference Fourier calculations, and the others were introduced in calculated positions. The hydrogen atoms connected to C-10 and C-11 carbon atoms were not introduced in the calculations, owing to the difficulty of calculating the position of a hydrogen atom linked to a carbon atom showing an unusual bonding geometry. Table 2 contains a list of the coordinates of non-hydrogen atoms. Table 4 reports some statistical parameters obtained in the last refinement cycle.

The atomic scattering factors were taken from Ref. 35. The calculations were performed on an IBM 3081 computer of the Centro Nazionale Universitario di Calcolo Elettronico, CNUCE (Pisa). The programs PARST[36] and ORTEPII[37] were also used.

Additional material including H-atom coordinates, thermal parameters and a list of observed and calculated structure factors is available.

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