Studies in Crystal Engineering. Photochemical and Crystallographic Investigations of Bromocoumarins and (±)-7-(*p*-Bromobenzylidene)piperitone

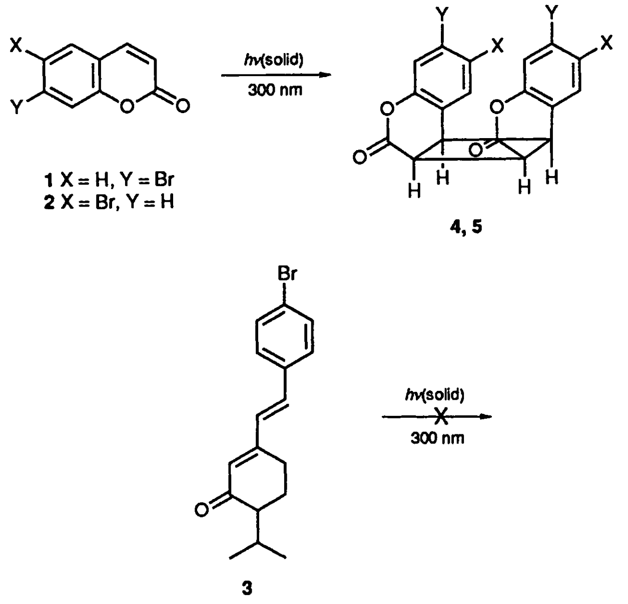
P. Venugopalan, T. Bharati Rao† and K. Venkatesan*
Department of Organic Chemistry, Indian Institute of Science, Bangalore-560 012, India

Photodimerisations of bromo-substituted coumarins **1** and **2** and (±)-7-(bromobenzylidene)piperitone **3** have been investigated in the solid state. 6-Bromocoumarin and 7-bromocoumarin crystals yield *syn* head-to-head dimers upon irradiation, whereas **3** is photostable. The photobehaviour of these systems is rationalised in terms of their crystal packing. The β steering ability of the bromo group has been examined for crystal engineering and the effect of the topological features of the organic moiety on the molecular packing is emphasised.

It is well known that, for photocyclodimerisation to take place in the solid state, the reactive partners must be within a distance of *ca.* 4.2 Å.[1-3] The central problem encountered in achieving cycloaddition reactions in the solid state is concerned with that of 'Crystal Engineering', namely to preorganise the reactive partners within the favourable distance.[4,5] In this context many steering groups such as chloro,[6-9] acetoxy,[10-11] sulphur,[12] methylenedioxy[13] *etc.* have been examined. It is noteworthy that, in the crystal structure of bromine, the Br ··· Br intermolecular contact is very much less (3.31 Å) than the sum of their van der Waals radii (3.90 Å).[14] The Cambridge data base analysis[15] also reveals the presence of this attractive and anisotropic intermolecular interaction in the crystal lattice. These observations could be used for generating photoreactions in a predictable manner. Indeed, a perusal of the work of Schmidt and colleagues[1-3] shows that all the bromocinnamic acids reported by them are β packed and photoreactive. However, the influence of the topological features of the organic moiety, namely the overall three dimensional shape of the molecule, on the desired molecular packing, even in the presence of steering groups, cannot be ignored, as was clear from the X-ray crystallographic investigations of *p*-chloro- and *o*-chlorobenzylidenepiperitones and their photobehaviour in the crystalline state.[16] It was considered worthwhile to investigate this aspect, namely the combined effects of steering groups and molecular topology on photo-behaviour in the solid state, by choosing appropriate organic systems. The two systems with different topological features but the same steering group chosen for detailed investigations were the planar bromocoumarins **1** and **2** and the non-planar 3-(*p*-bromophenylvinyl)-6-isopropylcyclohex-2-enone **3**. The results pertaining to their photobehaviour and nature of crystal packing are discussed in this paper.

Experimental

7-Bromocoumarin (**1** m.p. 82 °C) and 6-bromocoumarin, (**2**, m.p. 163 °C) were synthesised by the reported procedures[17] and crystallised from ethanol–chloroform mixture. Powdered samples of these compounds were irradiated in a Rayonet photochemical reactor (λ = 300 nm) at room temperature. The progress of the photoreaction was monitored by ^{1}H NMR spectroscopy and thin layer chromatography (TLC). Irradiation was continued until no further increase in the products occurred. The product dimers were separated by column chromatography (ethyl acetate–hexane, 20:80) and characterised by comparison of their spectral properties with similar coumarin dimers.[18-19] The dimer yields, as determined from ^{1}H NMR spectra, were as large as 90% in both **1** and **2** after 24 h of irradiation.



Scheme 1

3 was synthesised (m.p. 112 °C) by the method of Read and Smith[20] and crystallised from methanol–chloroform mixture. Irradiation under identical conditions did not yield any dimer. The observations are schematically represented in Scheme 1.

X-Ray Structural Analyses and Refinement.—Crystals suitable for X-ray diffraction studies of **1** and **3** were obtained from ethanol–chloroform mixture and methanol respectively by slow evaporation. Plate-like single crystals of **2** were obtained after various attempts, but the crystal quality was not satisfactory for single crystal structural studies. Hence only the cell dimensions and the space group were determined. The three dimensional intensity data of **1** and **3** were collected using an Enraf–Nonius CAD-4 diffractometer. The intensity of the three standard reflections, measured in both cases after every 2000 s of X-ray exposure, showed only statistical variations. Corrections were applied for Lorentz and polarisation factors and for absorption.[21] The structure of **1** was solved using MULTAN 80[22] and that of **3** by SHELXS 86.[23] SHELX 76[24] was used for blocked full-matrix least squares refinement. The final difference Fourier

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† *Present address:* Department of Organic Chemistry, Regional Research Labs, Trivandram, Kerala, India.

Table 1 Crystal data for compounds **1**, **2** and **3**

Compound	**1**	**2**	**3**
Mol. formula	$C_9H_5O_2Br$	$C_9H_5O_2Br$	$C_{17}H_{19}OBr$
M_r	225.0	225.0	319.2
Space group	$P2_12_12_1$	$P\bar{1}$ or $P1$	$P2_1/n$
a(Å)	4.313(2)	4.543(1)	12.469(3)
b	33.417(6)	5.867(1)	8.821(2)
c	5.617(3)	33.250(6)	28.427(5)
α/°	90	91.81(2)	90
β	90	91.63(2)	101.24(2)
γ	90	94.05(1)	90
V/Å^3	809.6(7)	883.3(1.2)	3066.5(10.4)
Z	4	4	8
D_x(Mg m^{-3})	1.846	1.692	1.383
D_m(Mg m^{-3})	1.83	1.68	1.38
Radiation	Cu-Kα	Cu-Kα	Mo-Kα
(Å)	1.5418	1.5418	0.7107
μ/mm^{-1}	6.13		2.59
F(000)	440		1312
Crystal size/mm	0.4 × 0.2 × 0.2	0.7 × 0.6 × 0.08	0.20 × 0.25 × 0.35
θ limit/°	60		25
Mode of data collection	ω/2θ		ω/2θ
Number of intensity controls	3		3
Number of reflections collected	809		4178
Number of observed reflections	703 ($\|F_o\| > 3\sigma\|F_o\|$)		2302 ($\|F_o\| > 4\sigma\|F_o\|$)
Final R^a	0.060		0.063
Weighted $R^a(R_w)$	0.068		0.067
Weighting Function (w)	$3.7219/[\sigma^2(\|F_o\|) + 0.001\,015\|F_o\|^2]$		$3.1868/[\sigma^2(\|F_o\|) + 0.001\,62\|F_o\|^2]$
Residual electron density/Å^{-3}	0.4		0.5
No. of variables	129		495

[a] $R = \Sigma|F_o - |F_c||/\Sigma F_o$; $Rw = \Sigma(w^{1/2}|F_o - |F_c||)/\Sigma(w^{1/2}F_o)$.

Table 2 Fractional atomic co-ordinates (× 10^4) of non-hydrogen atoms in **1**

Atom	x	y	z
Br(1)	7312(3)	2751(0)	2719(2)
C(2)	−238(28)	4409(3)	2936(16)
C(3)	839(33)	4579(3)	665(17)
C(4)	2842(30)	4382(3)	−674(16)
C(5)	6072(30)	3759(3)	−1376(16)
C(6)	7000(28)	3394(3)	−637(15)
C(7)	5928(28)	3246(3)	1542(18)
C(8)	3843(26)	3466(3)	2899(15)
C(9)	2909(25)	3831(3)	2148(13)
C(10)	3977(25)	3990(3)	−38(13)
O(1)	864(18)	4044(2)	3526(9)
O(2)	−2084(23)	4559(2)	4214(12)

map was featureless. The structural details and measurement conditions are given in Table 1. Anisotropic thermal parameters of non-hydrogen atoms, hydrogen atom-coordinates, bond lengths and bond angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC).*

Results and Discussion

The final positional coordinates of non-hydrogen atoms of **1** and **3** are given in Tables 2 and 3 respectively. The perspective views,[25] with atomic numbering, of the molecules **1** and **3** are depicted in Fig. 1 and 2 respectively. Their stereo packing diagrams[26] are shown in Figs. 3 and 4. The bond lengths and angles are depicted in Figs. 5 and 6 respectively.

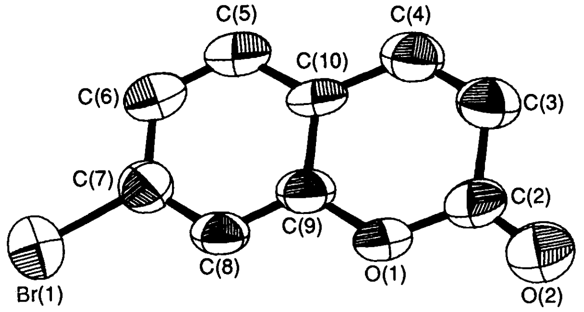

Fig. 1 Molecular structure of compound **1** with the numbering scheme

Irradiation of 7- and 6-bromocoumarins yielded *syn* head-to-head dimers **4** and **5**, whereas **3** was photostable in the crystalline state. The dimers can, in principle, adopt any one of four conformations: *syn* head-to-head, *syn* head-to-tail, *anti* head-to-head or *anti* head-to-tail. They were assigned as *syn* head-to-head by comparison with the spectral characteristics of related coumarin dimers.[18–19] It is clear from the packing diagram of **1** (Fig. 3) that the translationally related partners in the crystal lattice produce the dimer with a mirror symmetry, which confirms the conclusion derived from the spectral data.

In the case of a topochemical reaction, it would be expected that, before the reaction occurs, overlap of the π orbitals of the reactive partners should be favourable. If we define θ_1 as the rotation of one of the double bonds with respect to the other,

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* For details, see 'Instructions for Authors,' (1991), *J. Chem. Soc., Perkin Trans. 2*, in the January issue.

Table 3 Fractional atomic co-ordinates ($\times 10^4$) of non-hydrogen atoms in **3**

Atom	*x*	*y*	*z*
Molecule A			
Br(1)	3 957(1)	1 398(1)	307(0)
O(1)	−4 088(5)	1 608(8)	−2 525(2)
C(1)	1 337(7)	1 070(9)	−1 097(3)
C(2)	1 015(8)	1 208(10)	−668(3)
C(3)	1 781(8)	1 342(10)	−240(3)
C(4)	2 873(8)	1 249(9)	−267(3)
C(5)	3 205(7)	1 084(9)	−691(3)
C(6)	2 423(8)	991(10)	−1 108(3)
C(7)	564(8)	961(10)	−1 570(3)
C(8)	−496(8)	952(10)	−1 643(3)
C(9)	−1 248(7)	1 009(8)	−2 098(3)
C(10)	−827(7)	892(11)	−2 556(3)
C(11)	−1 724(7)	658(11)	−2 995(3)
C(12)	−2 698(7)	1 643(10)	−3 000(3)
C(13)	−3 118(8)	1 419(10)	−2 538(3)
C(14)	−2 299(8)	1 149(10)	−2 113(3)
C(15)	−3 583(8)	1 519(11)	−3 449(3)
C(16)	−3 231(10)	2 266(12)	−3 877(4)
C(17)	−4 005(9)	−65(12)	−3 557(4)
Molecule B			
Br(1)	5 298(1)	1 449(1)	1 528(0)
O(1)	13 094(5)	3 568(7)	4 400(2)
C(1)	7 986(7)	1 231(9)	2 919(3)
C(2)	8 216(7)	1 808(10)	2 496(3)
C(3)	7 427(9)	1 874(10)	2 085(3)
C(4)	6 398(8)	1 364(10)	2 091(3)
C(5)	6 146(7)	796(10)	2 508(4)
C(6)	6 937(8)	729(10)	2 908(3)
C(7)	8 828(8)	1 164(10)	3 365(3)
C(8)	9 774(7)	1 886(9)	3 456(3)
C(9)	10 544(7)	1 823(9)	3 909(3)
C(10)	10 359(7)	777(10)	4 297(3)
C(11)	11 386(9)	656(12)	4 697(3)
C(12)	12 038(7)	2 054(11)	4 830(3)
C(13)	12 275(7)	2 844(11)	4 392(3)
C(14)	11 420(7)	2 706(11)	3 962(3)
C(15)	12 988(7)	1 939(10)	5 249(3)
C(16)	12 649(10)	1 515(14)	5 712(4)
C(17)	13 877(10)	944(14)	5 140(4)

Table 4 Selected bond lengths (*a*) and angles (*b*) involving hydrogen atoms in 7-bromocoumarin with their esds in parentheses

(*a*)

Atoms	Distance /Å	Atoms	Distance/Å
C(3)–H(3)	1.09(6)	C(6)–H(6)	1.02(11)
C(4)–H(4)	1.23(7)	C(8)–H(8)	1.10(16)
C(5)–H(5)	0.94(11)		

(*b*)

Atoms	Angle/°	Atoms	Angle/°
C(2)–C(3)–H(3)	99(4)	C(10)–C(5)–H(5)	108(7)
C(4)–C(3)–H(3)	137(4)	C(5)–C(6)–H(6)	131(6)
C(3)–C(4)–H(4)	127(3)	C(7)–C(6)–H(6)	110(6)
C(10)–C(4)–H(4)	111(3)	C(7)–C(8)–H(8)	120(8)
C(6)–C(5)–H(5)	130(7)	C(9)–C(8)–H(8)	120(8)

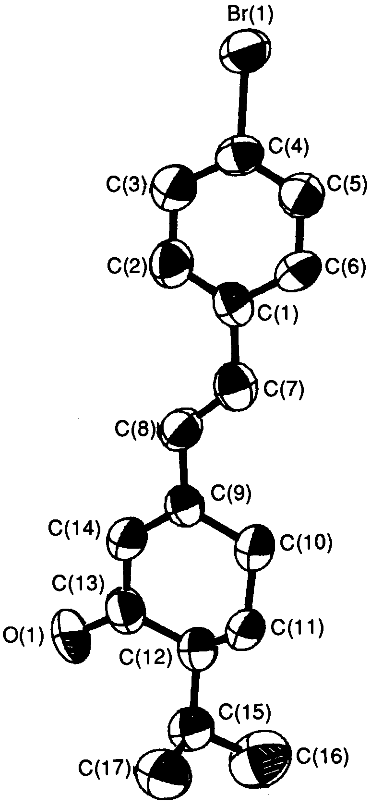


Fig. 2 Molecular structure of compound **3** with numbering scheme (both the molecules in the asymmetric unit are numbered in the same way)

Table 5 Selected bond lengths involving hydrogen atoms in (±)7-(*p*-bromobenzylidene)piperitone (molecules A and B) with their esds in parentheses

Molecule/A	Distance/Å	Molecule/B	Distance/Å
C(2)–H(2)	0.99(8)	C(2)–H(2)	0.84(8)
C(3)–H(3)	1.18(9)	C(3)–H(3)	1.01(6)
C(5)–H(5)	0.94(10)	C(5)–H(5)	0.98(6)
C(6)–H(6)	0.84(6)	C(6)–H(6)	0.95(10)
C(7)–H(7)	1.14(10)	C(7)–H(7)	0.86(6)
C(8)–H(8)	1.08(7)	C(8)–H(8)	0.88(6)
C(10)–H(101)	0.89(9)	C(10)–H(101)	0.91(9)
C(10)–H(102)	0.95(8)	C(10)–H(102)	1.14(10)
C(11)–H(111)	1.11(9)	C(11)–H(111)	0.83(12)
C(11)–H(112)	0.99(6)	C(11)–H(112)	1.04(7)
C(12)–H(12)	1.16(7)	C(12)–H(12)	1.27(11)
C(14)–H(14)	1.09(9)	C(14)–H(14)	0.84(6)
C(15)–H(15)	0.85(6)	C(15)–H(15)	1.04(10)
C(16)–H(161)	1.09(8)	C(16)–H(161)	1.05(8)
C(16)–H(162)	1.03(7)	C(16)–H(162)	1.08(9)
C(16)–H(163)	1.01(11)	C(16)–H(163)	0.99(8)
C(17)–H(171)	0.87(11)	C(17)–H(171)	1.06(6)
C(17)–H(172)	1.08(9)	C(17)–H(172)	1.04(6)
C(17)–H(173)	1.01(9)	C(17)–H(173)	1.16(6)

θ_2 as the angle of the parallelogram formed by the atoms of the double bonds C(3), C(4), C(4′) and C(3′) in **1** and θ_3 as a measure of the angle between the least squares planes through the atoms C(2), C(3), C(4) and C(10) and C(3), C(4), C(4′) and C(3′), their ideal values should be 0, 90 and 90° respectively (see Fig. 7). The displacement of the reactive partners, *d*, should be 0 Å. In the present case the calculated values are $\theta_1 = 0°$, $\theta_2 = 130.8°$, $\theta_3 = 89.6°$ and $d = 0.03$ Å. Thus there must be translational movement of the reactive partners to attain the ideal juxtaposition in the crystal lattice. It should be mentioned that in many cases the exact overlap of the π orbitals is never realised,[5] yet the photoreaction takes place with good yield. An outstanding example to be noted is the solid state photoreaction of 7-methoxycoumarin in which the reacting bonds are non-ideally oriented, with $\theta_1 = 65°$, yet the dimer yield is *ca.* 90%.[27] There are other examples known in the literature[28,29] emphasising the need for such motions to be invoked in rationalising dimerisation reactions in the crystalline state.

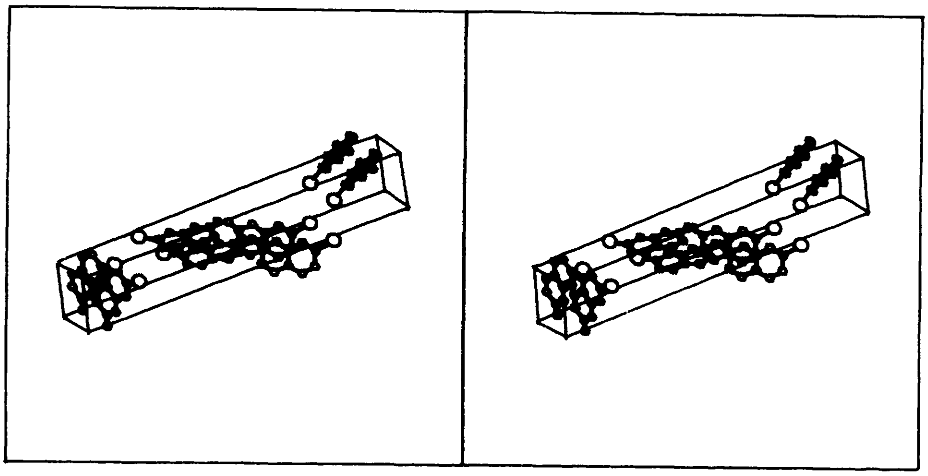


Fig. 3 Stereo view of the molecules of **1** in the unit cell

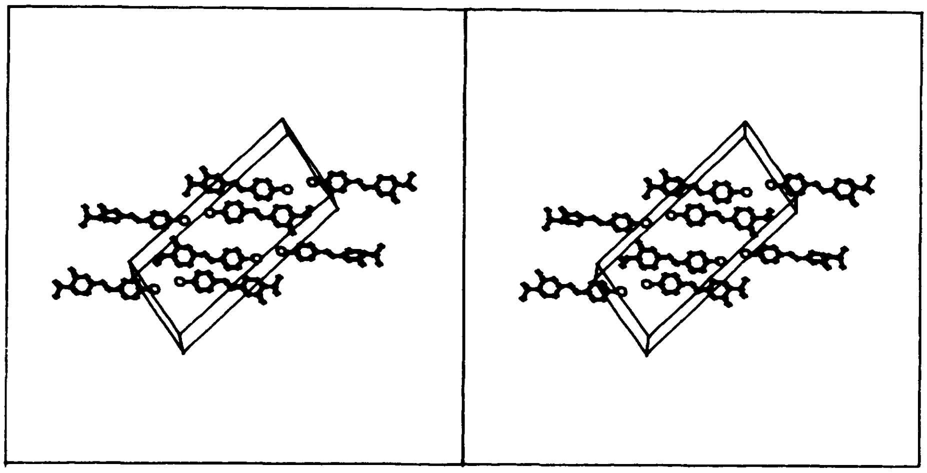


Fig. 4 Stereo view of the molecules of **3** in the unit cell

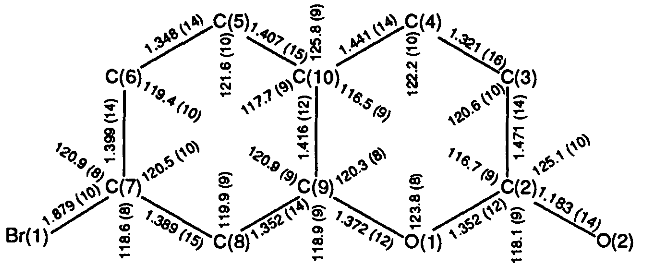
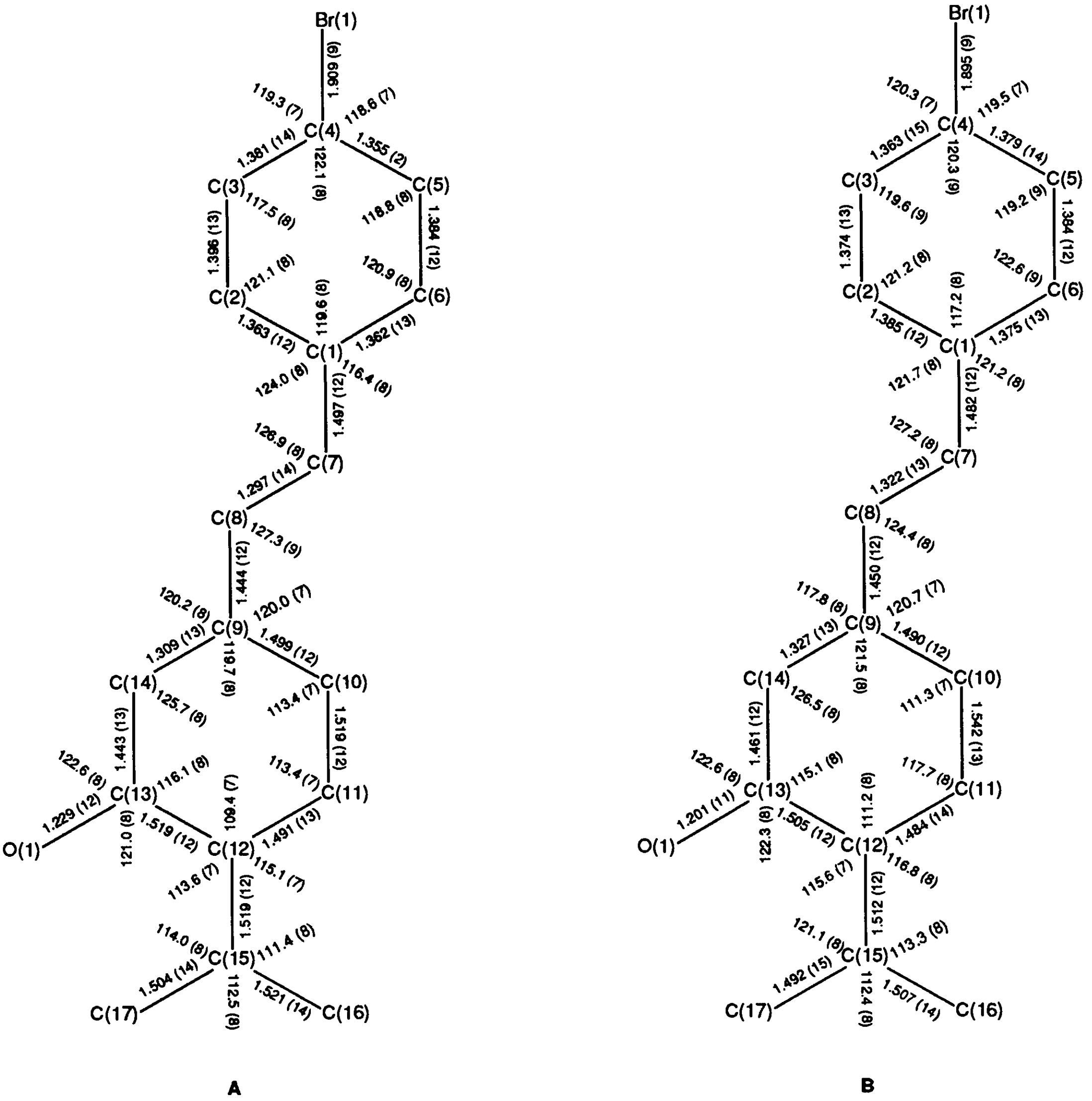


Fig. 5 Bond lengths/Å and angles/° of **1** with their esds in parentheses

Indeed, detailed lattice energy calculations performed for a large number of crystalline olefinic compounds have shown the importance of orientational flexibility and the influence of crystal environment towards the realisation of the photobehaviour.[27,30] Craig and co-workers have also carried out an incisive theoretical investigation, and showed that the short-term lattice instability created upon excitation has the effect of bringing one molecule close to its neighbour, promoting excimer of exciplex formation.[31] As a consequence of the increase in the attractive forces between the reactive molecules upon excitation, it may be supposed that the motion of the molecule necessary to achieve a maximum overlap becomes feasible.

From the packing of **3** (Fig. 4) it is clear that the double bonds are not suitably juxtaposed for dimerisation. There are two potentially reactive double bonds [C(7)=C(8) and C(9)=C(14)] in **3** which can, in principle, undergo dimerisation. There are cases of double dimerisation occurring in such instances.[32,33] As can be seen from the packing, the benzylic double bonds are too far away for any reaction. The potentially reactive double bonds [C(9)=C(14)], of the two crystallographically independent and antipodal molecules have the following intermolecular contacts: By the symmetry operation $[x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z]$ BC(14) comes close to AC(14) $[1 + x, y, 1 + z]$ (3.85 Å). However the counterpart, AC(9), is at a distance of 5.69 Å from BC(9), too far away to favour dimerisation. Thus neither double bond can undergo any dimerisation in the crystalline state.

The β steering ability of the bromo group was one motivating factor for studying the photobehaviour of these organic systems in the solid state. In the crystal structure of unsubstituted coumarin[34] the shortest axis is as long as 5.676(6) Å which would not allow it to react in a topochemical fashion to give a mirror symmetric product. On the other hand, bromo substitution at the 6- or 7-positions engineers the molecules to adopt β stack packing mode. The bromoacetyl coumarin[35] also stacks about the shortest repeat axis of 4.229(2) Å. It is also worth mentioning that both the photoreactive 6-chloro and 7-chlorocoumarins are also β stacked with repeat distances of 4.09 and 4.454 Å respectively.[9] The common feature of all these compounds is that they are all planar. Interestingly all five bromo-substituted *trans* cinnamic acids reported by Schmidt,[3] which are β stacked and photoreactive, are also essentially planar. The planarity of the molecules allows the additional π ··· π interactions to operate between the interstacks which results in the β packing. It seems relevant to add that, in



A

B

Fig. 6 Bond lengths/Å and angles/° of **3** with their esds in parentheses

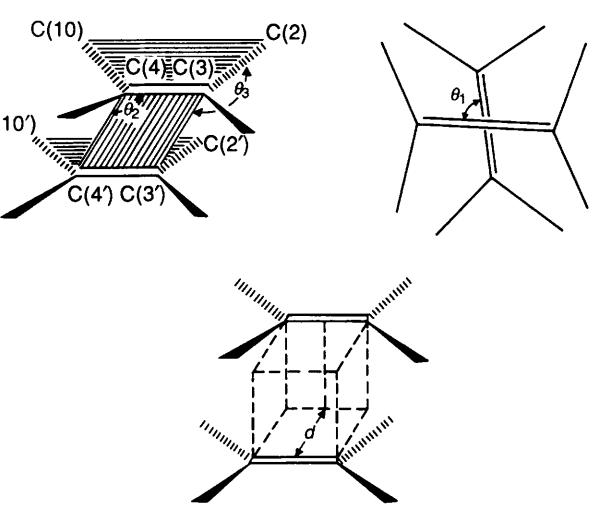


Fig. 7 Geometrical parameters used in the relative representation of the reactive double bonds

unsymmetrically substituted diolefinic compounds, the π ··· π interactions of the benzene ring or the N ··· N interactions of the pyrimidine ring also play an important role in the crystal packing.[36]

Cambridge Crystallographic Data Base analyses of Cl ··· Cl interactions in chloroaromatic structures reveal that the maximum number of short contacts are concentrated in the region 3.8–4.1 Å.[8] Even though the molecules form a β type packing in all these cases, the Cl ··· Cl distance is not less than the sum of the van der Waals radii. This indicates that the observed packing mode is the result of the combined effects of the π ··· π interactions and X ··· X interactions (X = halogen). In many of the crystal structures there may exist very close X ··· X contacts less than the sum of their van der Waals radii, between atoms related by symmetry elements other than translation along the shortest axis, *e.g.* 3.69 Å in 7-chlorocoumarin (van der Waals sum = 3.60 Å) and 3.75 Å in 7-bromocoumarin (van der Waals sum = 3.90 Å).

The failure to achieve the β packing mode in the case of (±)7-(*p*-bromobenzylidene)piperitone calls for an explanation. The molecules are quite non-planar, with the cyclohexenone ring of both molecules in a sofa conformation[37] (the torsional angles of interest are recorded in Fig. 8) and an isopropyl group which is quite anisotropic. This does not allow an efficient close packing in the β structure. It is noteworthy that there is a short Br ··· Br contact of 3.549 Å present between the independent molecules of the asymmetric unit. Even though the Br ··· Br interaction is operative in this crystal, owing to the nonplanar nature of the molecules, an energetically more favourable packing seems to be achieved in α packing rather than in the β type. In this connection it is noteworthy that the crystals of (±)7-(benzyl-

Table 6 Selected bond angles involving hydrogen atoms in (±)7-(*p*-bromobenzylidene)piperitone (molecules A and B) with their esds in parentheses

Molecule/A	Angle/°	Molecule/B	Angle/°
C(1)–C(2)–H(2)	132(5)	C(1)–C(2)–H(2)	119(5)
C(3)–C(2)–H(2)	105(5)	C(3)–C(2)–H(2)	119(5)
C(2)–C(3)–H(3)	128(4)	C(2)–C(3)–H(3)	118(4)
C(4)–C(3)–H(3)	114(4)	C(4)–C(3)–H(3)	122(3)
C(4)–C(5)–H(4)	106(6)	C(4)–C(5)–H(5)	113(4)
C(6)–C(5)–H(4)	134(6)	C(6)–C(5)–H(5)	127(4)
C(1)–C(6)–H(6)	122(4)	C(1)–C(6)–H(6)	111(6)
C(5)–C(6)–H(6)	117(4)	C(5)–C(6)–H(6)	127(4)
C(1)–C(7)–H(7)	116(5)	C(1)–C(7)–H(7)	99(4)
C(8)–C(7)–H(7)	116(5)	C(8)–C(7)–H(7)	133(4)
C(7)–C(8)–H(8)	116(4)	C(7)–C(8)–H(8)	115(4)
C(9)–C(8)–H(8)	117(4)	C(9)–C(8)–H(8)	121(4)
C(9)–C(10)–H(101)	113(6)	C(9)–C(10)–H(101)	109(6)
C(9)–C(10)–H(102)	108(5)	C(9)–C(10)–H(102)	120(5)
C(11)–C(10)–H(101)	100(6)	C(11)–C(10)–H(101)	101(6)
C(11)–C(10)–H(102)	95(5)	C(11)–C(10)–H(102)	109(6)
H(101)–C(10)–H(102)	125(8)	H(101)–C(10)–H(102)	105(7)
C(10)–C(11)–H(111)	113(5)	C(10)–C(11)–H(111)	105(8)
C(10)–C(11)–H(112)	114(4)	C(10)–C(11)–H(112)	110(4)
C(12)–C(11)–H(111)	95(5)	C(12)–C(11)–H(111)	99(8)
C(12)–C(11)–H(112)	102(4)	C(12)–C(11)–H(112)	113(4)
H(111)–C(11)–H(112)	118(6)	H(111)–C(11)–H(112)	111(9)
C(11)–C(12)–H(12)	88(4)	C(11)–C(12)–H(12)	78(5)
C(13)–C(12)–H(12)	109(4)	C(13)–C(12)–H(12)	116(5)
C(15)–C(12)–H(12)	119(4)	C(15)–C(12)–H(12)	114(5)
C(9)–C(14)–H(14)	111(5)	C(9)–C(14)–H(14)	122(4)
C(13)–C(14)–H(14)	123(5)	C(13)–C(14)–H(14)	112(4)
C(12)–C(15)–H(15)	102(4)	C(12)–C(15)–H(15)	103(6)
C(16)–C(15)–H(15)	99(4)	C(16)–C(15)–H(15)	119(6)
C(17)–C(15)–H(15)	117(4)	C(17)–C(15)–H(15)	95(6)
C(15)–C(16)–H(161)	96(4)	C(15)–C(16)–H(161)	110(4)
C(15)–C(16)–H(162)	121(4)	C(15)–C(16)–H(162)	105(5)
C(15)–C(16)–H(163)	113(6)	C(15)–C(16)–H(163)	113(4)
H(161)–C(16)–H(162)	119(6)	H(161)–C(16)–H(162)	125(6)
H(161)–C(16)–H(163)	102(7)	H(161)–C(16)–H(163)	103(6)
H(162)–C(16)–H(163)	104(7)	H(162)–C(16)–H(163)	100(6)
C(15)–C(17)–H(171)	103(7)	C(15)–C(17)–H(171)	110(3)
C(15)–C(17)–H(172)	109(5)	C(15)–C(17)– H(172)	110(3)
C(15)–C(17)–H(173)	109(5)	C(15)–C(17)–H(173)	108(3)
H(171)–C(17)– H(172)	112(9)	H(171)–C(17)– H(172)	109(5)
H(171)–C(17)–H(173)	129(9)	H(171)–C(17)–H(173)	107(4)
H(172)–C(17)–H(173)	95(7)	H(172)–C(17)–H(173)	113(5)

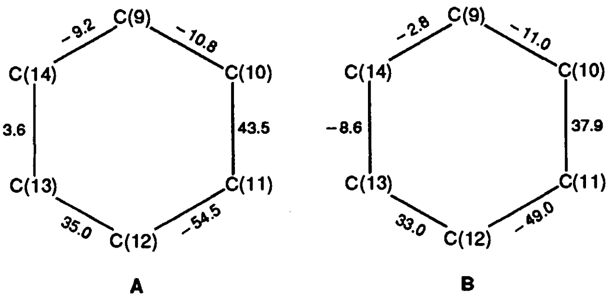


Fig. 8 Torsional angles of the cyclohexenone ring in **3**

idene)piperitone,[38] and its *para*-chloro and *ortho*-chloro derivatives,[16] adopt the same type of packing mode.

The significant conclusion emerging from the crystallographic and solid state photochemical studies of the bromo substituted compounds discussed in this paper and the related ones previously reported in the literature,[5,8,9,39] is that, when the halogen-substituted molecular moiety is planar β packing is favoured. If, on the other hand, the organic moiety is quite non-planar α packing mode appears more favourable. Thus, in efforts to preorganise molecules in the crystals in order to achieve the desired photodimerisation, the interplay between the subtle interactions, such as π···π interactions, of the organic moiety, and also its topological features, must be considered in addition to the attractive interactions of the steering groups.

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