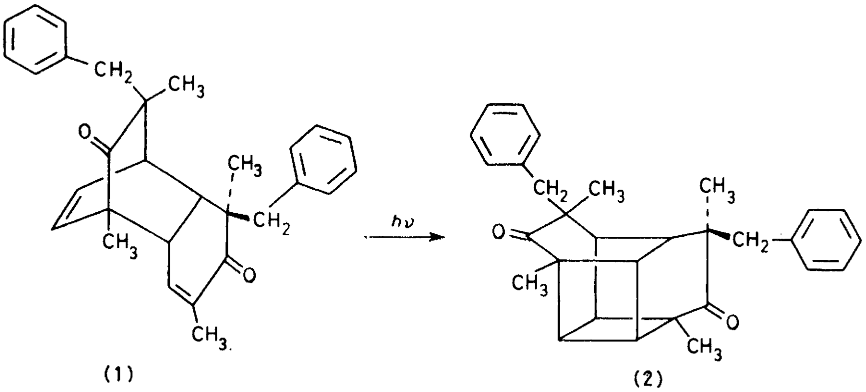
Carbonyl n–π^* Absorption Enhancement in β-Phenylketones: the Molecular Geometry of the 6-Benzyl-2,6-dimethylcyclohexa-2,4-dienone Diels–Alder Dimer and its Photocage Product

By **Hans-Dieter Becker,*** Department of Chemistry, Chalmers University of Technology and University of Gothenburg, S-412 96 Gothenburg, Sweden
Brian W. Skelton and **Allan H. White,*** Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia 6009, Australia

The molecular structures of the 6-benzyl-2,6-dimethylcyclohexa-2,4-dienone Diels–Alder dimer and its intramolecular photocycloaddition product have been determined by crystallographic methods. The enhancement of the n–π^* absorption in the u.v. spectrum of the photoproduct is discussed in terms of geometrically facilitated orbital interactions between the carbonyl group and its β-phenyl substituent.

CARBON alkylation of sodium 2,6-dimethylphenoxide with benzyl bromide gives 6-benzyl-2,6-dimethylcyclohexa-2,4-dienone which spontaneously dimerizes to give the ethano-bridged hydronaphthalene (1) by Diels–Alder reaction involving intermolecular addition of the γ, δ-bond across the diene system.[1] The gross skeletal structure of (1) was deducible by spectroscopic and photochemical means, but the stereochemistry at the disubstituted carbon atoms remained unknown.[2]



(1) (2)

In the u.v. spectrum of (1), the longest wavelength absorption due to the enhanced n–π^* transition of the carbonyl chromophore is unique in comparison to that of other cyclohexa-2,4-dienone dimers.[2,3] The very broad maximum extending to *ca.* 380 nm and showing some fine structure at *ca.* 315 nm, apparently derives from two overlapping transitions (see Figure 1). Upon irradiation ($\lambda > 340$ nm), (1) smoothly undergoes intramolecular cycloaddition to give the cage product (2).[2] In the ^{1}H n.m.r. spectrum of the photoproduct, the substituents are pair-wise equivalent due to the two-fold axis of symmetry of structure (2).

The electronic absorption spectrum of (2) is characterized by the disappearance of the n–π^* absorption of the cyclohexenone chromophore, and exhibition of the structured phenyl absorption hidden in the u.v. spectrum of (1). Remarkably, however, the expected decrease of the n–π^* absorption above 340 nm was found to be associated with an enhancement of the structured n–π^* absorption around 315 nm, suggestive of more favourable interaction of the carbonyl chromophore with the β-phenyl substituent in the photocage compound (see Figure 1).

An effect of the keto-group orientation, with respect to an aromatic ring, on the enhancement of the carbonyl n–π^* transition has previously been noted in the absorption spectra of 2-acetylbenzonorbornene epimers.[4,5] To gain some insight into the molecular geometry of (1) and (2), and to establish their stereo-

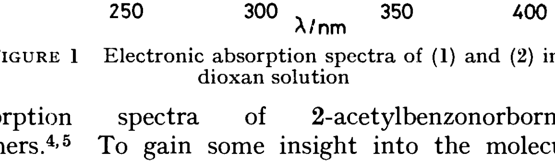


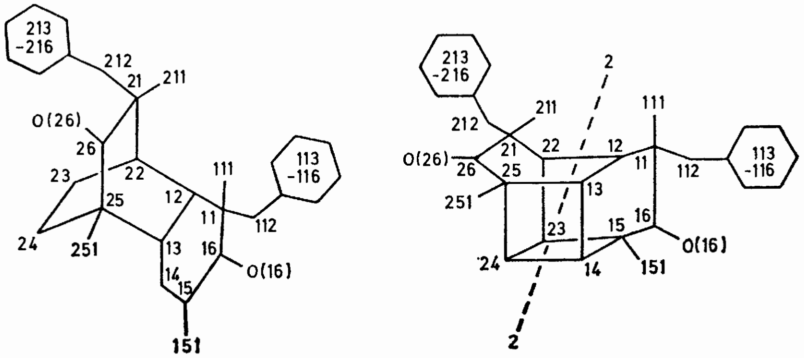
FIGURE 1 Electronic absorption spectra of (1) and (2) in dioxan solution

chemistry at the disubstituted sp^3 carbon atoms, we have carried out the *X*-ray structure analyses described in this paper.

CRYSTALLOGRAPHY

Crystal Data.—(1) $C_{30}H_{32}O_2$, $M = 424.6$, monoclinic, space group $P2_1/c$ (C_2^5h, No. 14), $a = 15.370(5)$, $b = 7.183(1)$, $c = 21.48(1)$ Å, $\beta = 99.87(7)°$, $U = 2\,336(3)$ Å^3, $Z = 4$, $D_m = 1.20(1)$ g cm^{-3}, $D_c = 1.21$ g cm^{-3}, $F(000) = 912$. Specimen: $0.08 \times 0.50 \times 0.01$ mm (needle). $\mu_{Cu} = 5.0$ cm^{-1}. (2) $C_{30}H_{32}O_2$, $M = 424.6$, monoclinic, space group $P2_1/n$ (C_{2h}^5, No. 14), $a = 13.05(1)$, $b = 18.81(2)$, $c = 9.659(4)$ Å, $\beta = 100.5(1)°$, $U = 2\,332(2)$ Å^3, $Z = 4$, $D_m = 1.21(1)$ g cm^{-3}, $D_c = 1.21$ g cm^{-3}, $F(000) = 912$. Specimen: $0.20 \times 0.03 \times 0.23$ mm (plate). $\mu_{Cu} = 5.0$ cm^{-1}.

Structure Determination.—Data acquisition: unique data sets were measured within the limit $2\theta_{max.}$ 100° on a Syntex $P\bar{1}$ four circle diffractomer; small specimen sizes necessitated the use of Ni-filtered Cu-K_α radiation (λ 1.541 8 Å) and the quality of the data was such that the application of correction for absorption, even though significant, was not felt justified. For (1) and (2), 2 396 and 2 383 independent reflections were measured; of these 837 and 976, respectively, were considered 'observed' at the $I > 3\sigma(I)$ level and used in the least-squares refinements after solution of the structures by direct methods. Least-squares refinement was basically 9×9 block diagonal least squares, with C and O thermally anisotropic. Hydrogen atom positional parameters were refined in the block of the parent carbon atom; U_H (isotropic) was constrained at $\langle 1.25\ U_{ii}$ (parent C)$\rangle$. Although overparametrized, both refinements proceeded smoothly and meaningfully. Residuals at convergence were (R,R',S): 0.086, 0.091, 2.6 (1); 0.066, 0.072, 1.9 (2), reflection weights being $[\sigma^2(F_o) + 0.000\,5(F_o)^2]^{-1}$. Scattering factors: neutral atom, C,O corrected for anomalous dispersion (f',f'').[6-8] Computation: *X*-RAY 76 program system,[9] CYBER 76 computer.



(1) **(2)**

SCHEME

Structure factor amplitudes, thermal parameters, and hydrogen atom geometries are in Supplementary Publication No. SUP 22966 (26 pp.).*

Skeletal atom numbering is as given in the Scheme; hydrogen atoms are numbered according to the parent carbon, suffixed A—C for distinguishing purposes as necessary. Results are given in the Tables and Figures.

RESULTS AND DISCUSSION

For both (1) and (2) bond lengths and interbond angles listed in Table 2 are imprecise; however, significant conclusions regarding the stereochemistry can be drawn from the analyses. Thus, the structure analysis of dimer (1) reveals that the Diels–Alder dimerization of 6-benzyl-2,6-dimethylcyclohexa-2,4-dienone involves a transition state in which the benzyl groups, being sterically more demanding than the geminal methyl substituents, are pointing outwards.[10] Consequently, in (1) the stereochemical orientation of the methyl groups at the disubstituted sp^3 carbon atoms differs from that of the structurally related Diels–Alder dimer of 6-hydroxy-2,6-dimethylcyclohexa-2,4-dienone.[11]

Annelation appears to have little effect on the geometry of the bicyclo[2.2.2]octene moiety of (1). The dihedral angles between the C_2 bridges are similar to those found in some bicyclo[2.2.2]octenes analysed recently.[12] For (1), least-squares planes have been calculated for the sequences (i) C(22), C(23), C(24), C(25), (ii) C(21), C(22), C(25), C(26), (iii) C(12), C(22), C(25), C(13): σ (defining atoms) for the three planes are 0.00, 0.03, and 0.01 Å, respectively. The dihedral angles between the planes are 119.8 [(i)/(ii)], 121.2 [(i)/(iii)], and 119.1: [(ii)/(iii). The 'plane' (iv) through C(11),—C(14) has σ (defining atoms) 0.08 Å, and the dihedral angle between (iii) and (iv) is 127.6°.

The geometry of the cyclohexenone moiety of (1) is remarkable insofar as the ring conformation is that of a fairly flat boat. A least-squares plane calculated through C(11)—C(16) has σ (defining atoms) 0.21 Å. Individual defining atom deviations are [C(11)—C(16), respectively, −0.33, 0.18, 0.06, −0.16, 0.03, and 0.22 Å; see also Figure 2(a)]. The dihedral angle between the plane of the carbonyl group and that of the β-carbon carrying the phenyl substituent is as large as 98.6°. By contrast, the corresponding dihedral angle involving the homoconjugated carbonyl group C(26)=O(26) is 62.2° (see Table 3).

The more complex fused ring structure of (2) evidences more strain generally. The two four-membered rings C(13), C(14), C(24), C(25) and C(23), C(24), C(14), C(15)

---

* For details see Notice to Authors No. 7, *J.C.S. Perkin II*, 1979, Index issue.

TABLE 1

Non-hydrogen atom fractional cell co-ordinates for (1) and (2)

		(1)	
Atom	*x*/*a*	*y*/*b*	*z*/*c*
C(11)	0.162 4(10)	0.337 0(20)	0.083 1(7)
C(111)	0.203 5(14)	0.508 4(24)	0.055 7(9)
C(112)	0.086 7(11)	0.269 0(25)	0.033 0(9)
C(113)	0.112 3(10)	0.186 3(21)	−0.026 6(7)
C(114)	0.116 3(18)	0.304 6(26)	−0.077 1(8)
C(115)	0.144 0(19)	0.230 0(37)	−0.131 2(8)
C(116)	0.165 8(13)	0.047 7(25)	−0.134 6(9)
C(117)	0.161 7(15)	−0.071 9(27)	−0.085 7(10)
C(118)	0.132 3(13)	0.001 2(25)	−0.033 1(7)
C(12)	0.230 3(10)	0.194 0(20)	0.105 5(6)
C(13)	0.195 6(11)	0.036 2(22)	0.149 3(7)
C(14)	0.112 8(11)	0.089 2(24)	0.174 8(8)
C(15)	0.081 8(10)	0.261 4(21)	0.175 4(7)
C(151)	0.002 8(17)	0.322 4(38)	0.205 5(10)
C(16)	0.117 0(12)	0.417 1(23)	0.136 6(8)
O(16)	0.101 2(8)	0.575 7(16)	0.145 7(5)
C(21)	0.386 5(9)	0.088 9(21)	0.138 9(6)
C(211)	0.386 5(15)	−0.004 9(28)	0.072 0(8)
C(212)	0.482 0(11)	0.129 0(24)	0.170 5(7)
C(213)	0.527 5(11)	0.278 7(24)	0.135 1(6)
C(214)	0.521 5(13)	0.462 3(26)	0.143 3(7)
C(215)	0.565 1(14)	0.593 1(26)	0.110 9(9)
C(216)	0.613 1(14)	0.531 8(25)	0.068 3(8)
C(217)	0.624 3(15)	0.348 5(27)	0.057 0(8)
C(218)	0.579 1(16)	0.219 4(24)	0.091 0(10)
C(22)	0.321 9(10)	0.255 0(19)	0.132 7(7)
C(23)	0.321 4(11)	0.321 3(23)	0.202 3(7)
C(24)	0.294 9(12)	0.188 6(25)	0.237 3(6)
C(25)	0.271 6(10)	0.003 7(19)	0.208 3(6)
C(251)	0.248 4(14)	−0.145 1(31)	0.255 7(8)
C(26)	0.350 6(11)	−0.057 0(22)	0.181 0(8)
O(26)	0.383 6(8)	−0.209 7(15)	0.189 1(5)
		(2)	
	x/*a*	*y*/*b*	*z*/*c*
C(11)	0.464 3(7)	0.325 8(5)	0.477 5(9)
C(111)	0.425 7(10)	0.402 4(6)	0.448 4(13)
C(112)	0.557 4(9)	0.309 6(5)	0.400 0(12)
C(113)	0.643 4(8)	0.363 9(5)	0.426 2(10)
C(114)	0.718 1(8)	0.362 8(6)	0.546 2(11)
C(115)	0.800 6(10)	0.411 2(7)	0.571 6(13)
C(116)	0.802 9(10)	0.464 2(6)	0.470 9(13)
C(117)	0.729 5(9)	0.464 3(6)	0.346 4(13)
C(118)	0.649 6(10)	0.414 8(6)	0.325 2(12)
C(12)	0.490 7(7)	0.310 8(5)	0.640 2(8)
C(13)	0.537 9(8)	0.234 9(5)	0.667 7(10)
C(14)	0.458 4(9)	0.181 1(5)	0.593 5(11)
C(15)	0.357 8(7)	0.214 9(5)	0.514 8(9)
C(151)	0.275 9(11)	0.160 8(6)	0.444 5(12)
C(16)	0.377 4(7)	0.273 7(5)	0.417 9(9)
O(16)	0.330 9(5)	0.279 4(4)	0.297 7(6)
C(21)	0.420 7(7)	0.320 4(5)	0.865 8(10)
C(211)	0.464 3(10)	0.395 3(6)	0.907 7(12)
C(212)	0.326 8(8)	0.305 9(6)	0.943 0(10)
C(213)	0.239 0(7)	0.360 9(5)	0.918 8(9)
C(214)	0.236 2(9)	0.414 5(6)	1.021 2(11)
C(215)	0.158 6(11)	0.466 0(6)	1.002 9(16)
C(216)	0.086 1(10)	0.466 1(7)	0.881 3(14)
C(217)	0.086 0(9)	0.413 2(7)	0.779 0(12)
C(218)	0.161 3(8)	0.362 3(6)	0.799 5(11)
C(22)	0.389 4(8)	0.311 2(5)	0.704 0(10)
C(23)	0.338 9(8)	0.240 9(5)	0.663 7(9)
C(24)	0.414 8(9)	0.178 5(5)	0.732 4(11)
C(25)	0.517 5(7)	0.206 8(5)	0.818 1(9)
C(251)	0.591 8(11)	0.149 8(7)	0.878 2(14)
C(26)	0.501 9(9)	0.263 6(6)	0.920 3(9)
O(26)	0.549 3(6)	0.265 3(4)	1.040 4(7)

TABLE 2

Molecular non-hydrogen geometry. Primed atoms lie in the other half of the molecule

	(1)		(2)	
Atoms	*n* = 1	*n* = 2	*n* = 1	*n* = 2
Distances (Å)				
C(*n*1)–C(*n*2)	1.48(2)	1.54(2)	1.57(1)	1.55(2)
C(*n*1)–C(*n*11)	1.55(2)	1.59(2)	1.53(2)	1.55(2)
C(*n*1)–C(*n*12)	1.52(2)	1.53(2)	1.57(1)	1.57(1)
C(*n*1)–C(*n*6)	1.55(2)	1.55(2)	1.53(1)	1.53(1)
C(*n*2)–C(*n*3)	1.62(2)	1.57(2)	1.56(1)	1.50(1)
C(*n*2)–C(*n*′2)	1.49(2)		1.56(1)	
C(*n*3)–C(*n*4)	1.52(3)	1.32(2)	1.53(1)	1.60(1)
C(*n*3)–C(*n*′5)	1.59(2)		1.61(1)	1.58(1)
C(*n*4)–C(*n*5)	1.33(2)	1.48(2)	1.53(1)	1.54(1)
C(*n*4)–C(*n*′4)			1.55(2)	
C(*n*5)–C(*n*6)	1.55(2)	1.50(2)	1.50(1)	1.49(1)
C(*n*5)–C(*n*51)	1.53(3)	1.56(3)	1.54(2)	1.49(2)
C(*n*6)–O(*n*6)	1.19(2)	1.21(2)	1.21(1)	1.21(1)
C(*n*12)–C(*n*13)	1.52(2)	1.55(2)	1.51(1)	1.53(1)
C(*n*13)–C(*n*14)	1.39(2)	1.34(3)	1.37(1)	1.42(1)
C(*n*13)–C(*n*18)	1.38(2)	1.40(3)	1.38(2)	1.39(1)
C(*n*14)–C(*n*15)	1.41(3)	1.41(3)	1.40(2)	1.39(2)
C(*n*15)–C(*n*16)	1.36(3)	1.35(3)	1.40(2)	1.37(2)
C(*n*16)–C(*n*17)	1.37(3)	1.35(3)	1.39(2)	1.40(2)
C(*n*17)–C(*n*18)	1.39(3)	1.43(3)	1.39(2)	1.36(2)
Angles (°)				
C(*n*2)–C(*n*1)–C(*n*11)	111(1)	110(1)	110.9(8)	112.5(8)
C(*n*2)–C(*n*1)–C(*n*12)	115(1)	116(1)	113.2(7)	111.9(7)
C(*n*2)–C(*n*1)–C(*n*6)	113(1)	107(1)	105.8(7)	107.9(8)
C(*n*11)–C(*n*1)–C(*n*12)	107(1)	109(1)	110.7(9)	108.5(8)
C(*n*11)–C(*n*1)–C(*n*6)	105(1)	107(1)	109.6(8)	110.3(8)
C(*n*12)–C(*n*1)–C(*n*6)	105(1)	106(1)	106.3(7)	105.5(8)
C(*n*1)–C(*n*2)–C(*n*3)	113(1)	105(1)	110.0(7)	112.6(8)
C(*n*1)–C(*n*2)–C(*n*′2)	119(1)	111(1)	110.4(7)	108.2(7)
C(*n*3)–C(*n*2)–C(*n*′2)	111(1)	108(1)	105.9(8)	105.1(8)
C(*n*2)–C(*n*3)–C(*n*4)	114(1)	112(1)	108.2(2)	109.2(8)
C(*n*2)–C(*n*3)–C(*n*′5)	107(1)		109.1(8)	112.0(8)
C(*n*4)–C(*n*3)–C(*n*′5)	107(1)		89.8(7)	87.8(7)
C(*n*3)–C(*n*4)–C(*n*5)	124(2)	119(1)	113.9(8)	112.5(8)
C(*n*3)–C(*n*4)–C(*n*′4)			86.6(8)	85.1(7)
C(*n*5)–C(*n*4)–C(*n*′4)			91.5(8)	92.0(8)
C(*n*4)–C(*n*5)–C(*n*6)	121(2)	106(1)	112.9(8)	113.3(9)
C(*n*4)–C(*n*5)–C(*n*51)	126(2)	114(1)	114.1(8)	113.7(9)
C(*n*6)–C(*n*5)–C(*n*51)	113(2)	110(1)	113.2(8)	114.5(8)
C(*n*4)–C(*n*5)–C(*n*′3)		107(1)	86.5(7)	84.2(7)
C(*n*6)–C(*n*5)–C(*n*′3)		105(1)	114.4(8)	115.2(8)
C(*n*51)–C(*n*5)–C(*n*′3)		114(1)	113.2(9)	112.5(9)
C(*n*5)–C(*n*6)–C(*n*1)	112(1)	115(1)	115.8(7)	116.2(7)
C(*n*5)–C(*n*6)–O(*n*6)	120(2)	124(2)	123.4(8)	123.0(10)
O(*n*6)–C(*n*6)–C(*n*1)	127(2)	121(2)	120.7(9)	120.9(9)
C(*n*1)–C(*n*12)–C(*n*13)	116(1)	113(1)	113.9(9)	115.9(8)
C(*n*12)–C(*n*13)–C(*n*14)	118(1)	125(2)	121.7(9)	119.2(8)
C(*n*12)–C(*n*13)–C(*n*18)	124(1)	118(1)	119.3(9)	123.5(9)
C(*n*14)–C(*n*13)–C(*n*18)	118(1)	117(2)	119.0(10)	117.3(9)
C(*n*13)–C(*n*14)–C(*n*15)	118(1)	123(2)	123.0(11)	121.2(10)
C(*n*14)–C(*n*15)–C(*n*16)	121(2)	119(2)	117.2(10)	119.0(12)
C(*n*15)–C(*n*16)–C(*n*17)	121(2)	123(2)	120.1(11)	121.1(12)
C(*n*16)–C(*n*17)–C(*n*18)	117(2)	117(2)	120.5(11)	119.2(10)
C(*n*17)–C(*n*18)–C(*n*13)	124(2)	122(2)	120.0(10)	122.2(10)

TABLE 3

Dihedral angles (°) between the carbonyl groups and their β-carbon atoms in (1) and (2) (see Figure 3)

Plane defining atoms	Plane	Angle between	(1)	(2)
O(16), C(16), C(11)	a	a/b	98.6	69.6
C(112), C(16), C(11)	b	a/c	14.2	50.0
C(111), C(16), C(11)	c	b/c	112.8	119.6
O(26), C(26), C(21)	d	d/e	62.2	70.1
C(212), C(26), C(21)	e	d/f	54.6	46.7
C(211), C(26), C(21)	f	e/f	116.8	116.8

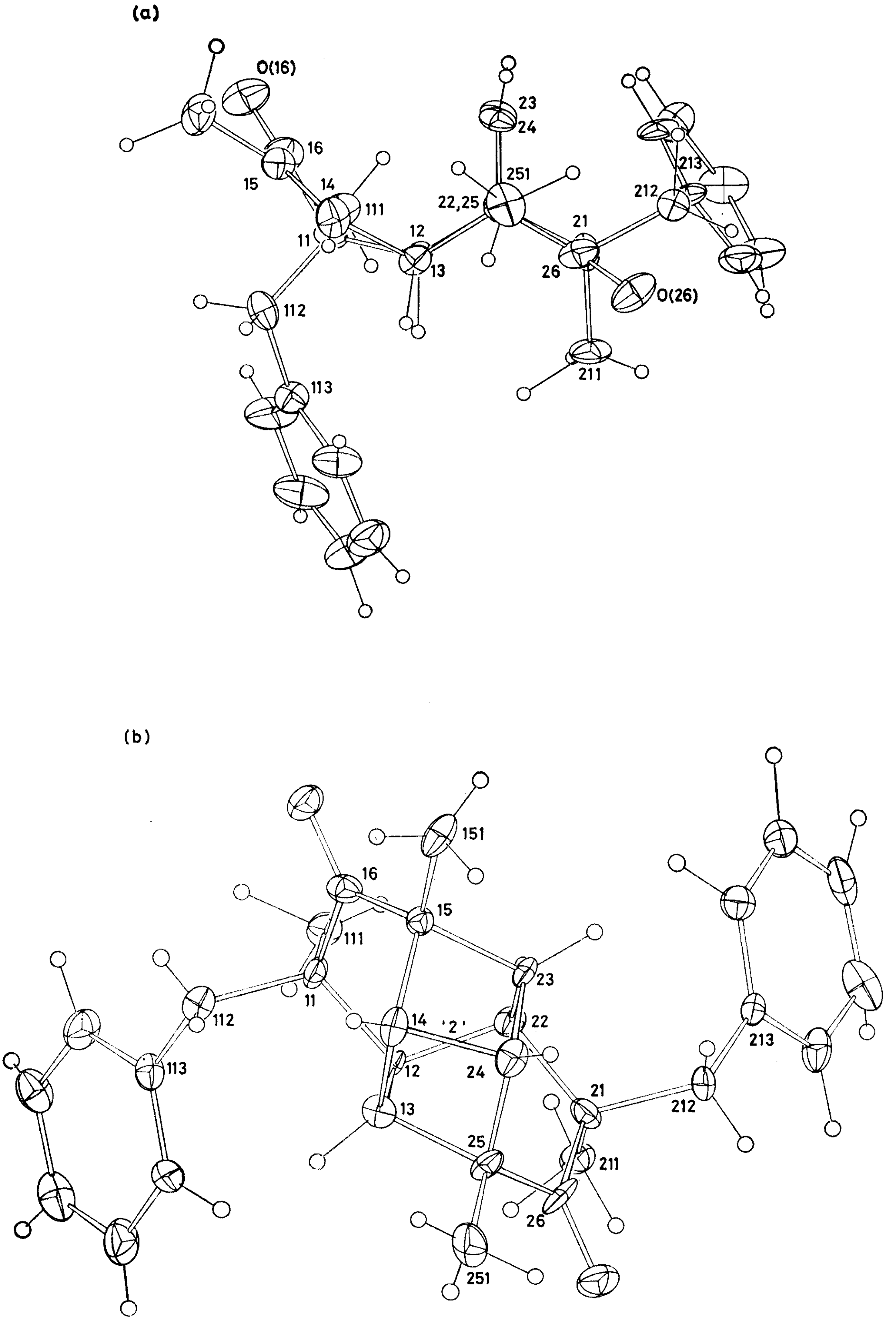


FIGURE 2 Molecular projections of (a) (1) and (b) (2). Carbon atom labelling is shown with 20% thermal ellipsoids for the non-hydrogen atoms. Hydrogen atoms are given an arbitrary radius of 0.1 Å.

have σ (defining atoms) for their planes of 0.16 and 0.18 Å, respectively, and the internal angle sums are 352.5 and 351.0°. The dihedral angle between the two four membered rings is 108.3°.

Formation of the C(14)–C(24), and C(15)–C(23) bonds by photochemical cycloaddition of (1) to give (2) considerably increases the 'boat' characteristic of the former cyclohexenone ring C(11)—C(16), [see Figure 2(b)]. A least-squares plane calculated through C(11)—C(16) has σ (defining atoms) 0.35 Å, individual deviations [C(11)—C(16), respectively] being 0.30, −0.49, 0.20, 0.24, −0.39, and 0.15 Å. The corresponding values for its C_2 symmetrical ring C(21)—C(26) are σ 0.33 Å, δ −0.27, 0.45, −0.18, −0.23, 0.38, and −0.14 Å [see Figure 2(b)].

Significantly, compared to the geometry of the C(16)=O(16) keto-group in dimer (1), in the photocage compound (2) the angle between the plane of the carbonyl group C(16)=O(16) and that of the β-carbon C(112) carrying the phenyl substituent has decreased to 69.6° (see Table 3). Thus, the photochemical conversion of (1) into (2) is associated with a fairly drastic change of one carbonyl group geometry and, consequently, the increase in the degree of enhancement of the structured n–π* absorption in the u.v. spectrum of (2) indeed appears to be attributable to geometrically more favourable π-orbital interactions between the carbonyl group and its β-phenyl substituent.

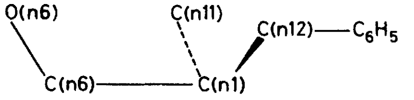


FIGURE 3 Carbonyl group geometry discussed in Table 3

We thank Dr. F. R. Hewgill for helpful discussions.

[0/544 *Received*, 11*th April*, 1980]

REFERENCES

[1] D. Y. Curtin, R. J. Crawford, and M. Wilhelm, *J. Am. Chem. Soc.*, 1958, **80**, 1391.

[2] (*a*) H.-D. Becker, and A. Konar, *Tetrahedron Lett.*, 1972, 5177; (*b*) H.-D. Becker, *Liebigs Ann. Chem.*, 1973, 1675.

[3] E. Adler, J. Dahlen, and G. Westin, *Acta Chem. Scand.*, 1960, **14**, 1580.

[4] R. R. Sauers and A. M. DePaolis, *J. Org. Chem.*, 1973, **38**, 639; 1974, **39**, 1850.

[5] For a comprehensive review, see K. N. Houk, *Chem. Rev.*, 1976, **76**, 1.

[6] D. T. Cromer and J. B. Mann, *Acta Crystallogr.*, 1968, *A***24**, 321.

[7] D. T. Cromer, and D. Liberman, *J. Chem. Phys.*, 1970, **53**, 1891.

[8] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

[9] 'The *X*-RAY System—Version of March 1976,' Technical Report TR-446, Computer Science Centre, University of Maryland, ed. J. M. Stewart.

[10] For a discussion of this subject, see E. Adler, S. Brasen, and H. Miyake, *Acta Chem. Scand.*, 1971, **25**, 2055.

[11] E. Adler and K. Holmberg, *Acta Chem. Scand.*, 1974, **28**, 465; and references cited therein.

[12] H.-D. Becker, B. Ruge, B. W. Skelton, and A. H. White, *Aust. J. Chem.*, 1979, **32**, 1231, 1687.