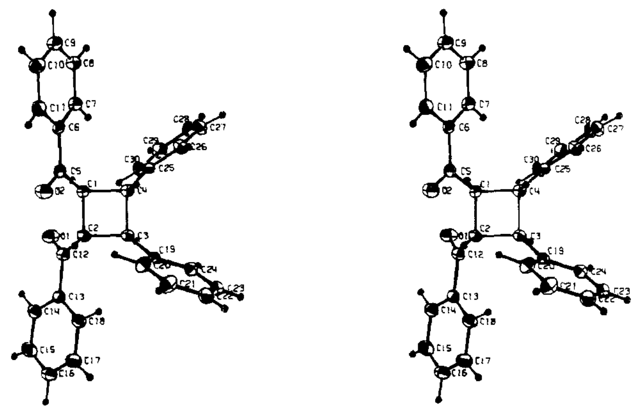


Figure 1. Stereoscopic view of a single molecule of **2**.

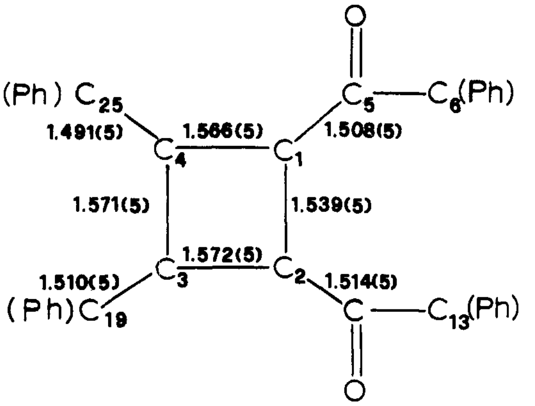
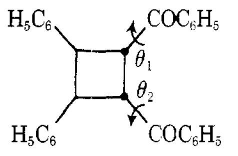


Figure 2. Selected bond distances and partial numbering scheme.

undertaken. The relative stereochemistry found in this study shows a δ-truxinic structure **2**, thus our previous assignment of structure **1** was incorrect.



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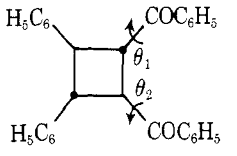

2

The three-dimensional structure of this photodimer of chalcone (mp 126 °C) was determined by x-ray structure analysis of crystals obtained from ethyl alcohol solution. A single colorless crystal was used to collect 2056 observed reflections with $2\theta < 130°$ on a Syntex $P2_1$ diffractometer (Cu Kα radiation). The space group is monoclinic, $P2_1/c$, with four molecules per unit cell: a = 10.902 (4) Å; b = 9.671 (4) Å; c = 21.426 (6) Å; and β = 90.69 (3)°; ρ_{obsd} = 1.22 g cm^{-3}; ρ_{calcd} = 1.222 g cm^{-3}. The structure was solved by direct methods[5] and refined by full-matrix least squares (for all nonzero reflections) to an unweighted R factor of 0.059 and a weighted R factor of 0.057.[6] Anisotropic temperature factors were used for all non-hydrogen atoms.

A stereoscopic drawing of one molecule is shown in Figure 1; bond distances in the ring and a partial numbering scheme are given in Figure 2. The bond lengths and bond angles are in general close to accepted values. Remarkably, bond lengths C2–C3, C3–C4, and C1–C4 are longer than normal C–C single bonds but their values are not unusual in substituted cyclobutanes.[3,4] There are no close contacts between molecules in the crystal.

The four-membered ring is slightly nonplanar; the torsion angles are in fact C1–C2–C3–C4 7.23°, C1–C4–C3–C2 −7.10°, C2–C1–C4–C3 7.25°, and C3–C2–C1–C4 −7.25°. Hence no other structures have been reported with an intermediate degree of puckering, i.e., in the range 1–18°.[4]

Torsion angles of the two benzoyl groups are C2–C1–C5–C6 176.58° and C1–C2–C12–C13 −172.83°, while torsion angles of the two phenyl groups are C1–C4–C25–C26 139.12° and C2–C3–C19–C20 −28.82°. Angle ABCD is considered positive if, when looking along the B–C bond, A has to be rotated clockwise to eclipse B, according to a well-known convention.[7]

The intramolecular nonbonded distance O1- - -O2 is 4.31 Å.

The preferred conformation is thus well inside the energetically allowed area generated as a function of the internal rotation angles θ_1 and θ_2 of the benzoyl groups in an energy exclusion map.[8]

Acknowledgments. We thank Professor I. C. Paul, Department of Chemistry, University of Illinois, Urbana, for the use of facilities in his x-ray laboratory.

Registry No.—**2,** 24825-07-8.

Supplementary Material Available: Tables of atomic coordinates in fractions of the unit cell parameters, bond lengths, and bond angles (5 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) University of Catania; (b) University of Illinois.
(2) G. Montaudo and S. Caccamese, *J. Org. Chem.*, **38,** 710 (1973).
(3) T. N. Margulis, *J. Am. Chem. Soc.*, **93,** 2193 (1971).
(4) F. A. Cotton and B. A. Frenz, *Tetrahedron*, **30,** 1587 (1974).
(5) The structure was solved by a version of the MULTAN program of G. Germain, P. Main, and M. M. Woolfson, *Acta Crystallogr., Sect. A*, **27,** 368 (1971), that has been incorporated into the SYNTEX EXTL system, based on the Data General Eclipse Computer.
(6) See the paragraph at the end of the paper regarding supplementary material.
(7) W. Klyne and V. Prelog, *Experientia*, **16,** 521 (1960).
(8) S. Caccamese and G. Montaudo, unpublished data.

Carbon Acidity. 57. Equilibrium Acidities of *o*- and *p*-Benzylbiphenyl. Steric Inhibition of Acidity

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We have previously reported[1] a number of relative ion pair acidities (pK_{CsCHA}) based on competitive equilibria with cesium cyclohexylamide (CsCHA) in cyclohexylamine (CHA).

$$R_1H + R_2^-Cs^+ \rightleftarrows R_1^-Cs^+ + R_2H \quad (1)$$

$$K = [R_2H][R_1^-Cs^+]/[R_1H][R_2^-Cs^+] \quad (2)$$

$$\log K = pK(2) - pK(1) \quad (3)$$

We report in this note the pK_{CsCHA} values obtained for the title hydrocarbons.[2] The results provide an assessment of the *o*-phenyl steric effect on the carbon acidity of diarylmethanes.[3]

Results and Discussion

Spectral data not reported previously are summarized in Table I. Table II gives results for the individual equilibrium runs.

Table I. Absorption Maxima for Cesium Salts in Cyclohexylamine

Hydrocarbon	λ_{max}, nm	$10^{-3}\epsilon$
o-BBP (*o*-benzylbiphenyl)	460	36.0 ± 1.4
p-BBP (*p*-benzylbiphenyl)	525	65.0 ± 2.7

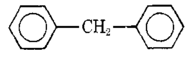
0022-3263/78/1943-2704$01.00/0

Table II. Summary of Equilibrium Constants

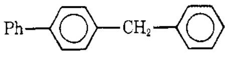
R_1H[a]	R_2H[a]	K	log K	n[b]	pK (per H)[c]
TPM	*p*-BBP	1.47 ± 0.28	0.17 ± 0.07	10	31.92 ± 0.12[d]
DCH	*p*-BBP	3.26 ± 0.37	0.51 ± 0.05	6	31.72 ± 0.14[d]
p-BBP	*o*-BBP	50.30 ± 12.7	1.69 ± 0.11	6	33.51 ± 0.12[e]
T*p*TM	*o*-BBP	1.46 ± 0.45	0.16 ± 0.13	8	33.50 ± 0.14[e]

[a] Abbreviations and pK_{CsCHA} values for indicators used are as follows: TPM, triphenylmethane, 31.45; T*p*TM, tri-*p*-tolylmethane, 33.04; DCH, 5*H*-dibenzo[*a*,*d*]cyclohepta-1,3-diene, 31.21. [b] Number of determinations. [c] pK of R_2H followed by the accumulated probable error, relative to pK_{CsCHA} (9-phenylfluorene) = 18.49. [d] Weighted average pK_{CsCHA} of *p*-BBP is 31.82 ± 0.12. [e] Weighted average pK_{CsCHA} of *o*-BBP is 33.51 ± 0.12.

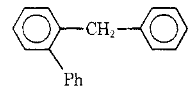
Table III. Effect of *p*-Phenyl Substituents on pK_{CsCHA} of Arylmethanes[a]



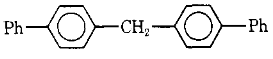
DPM; 33.4[b]



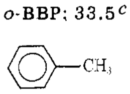
p-BBP; 31.8[c]



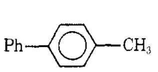
o-BBP; 33.5[c]



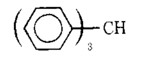
DBM; 30.8[b]



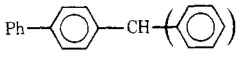
toluene; (41.2)[d,e]



p-MB;[e] 39.0[b,e]



TPM; 31.4[b]



BDPM;[e] 30.2[b]

[a] pK_{CsCHA} per hydrogen. Abbreviations used are as follows: *p*-MB, *p*-methylbiphenyl; BDPM, *p*-biphenylyldiphenylmethane. [b] Reference 1b. [c] This work. [d] A. Streitwieser, Jr., M. R. Granger, F. Mares, and R. A. Wolf, *J. Am. Chem. Soc.*, **95,** 4257 (1973). [e] A. Streitwieser, Jr., and F. Guibe, *J. Am. Chem. Soc.*, in press.

The pK value of 31.82 obtained for *p*-benzylbiphenyl (*p*-BBP) appears reasonable in view of the pK's already reported for diphenylmethane (DPM) and di-*p*-biphenylylmethane (DBM)[1b] (Table III). The results show an expected attenuation of substituent effects: substitution of a phenyl group into the para position of toluene gives a pK decrease of 2.2, the first *p*-phenyl substituent in diphenylmethane gives a ΔpK of 1.6, and the second gives a further ΔpK of 1.0. For comparison, a single *p*-phenyl substituent in triphenylmethane (TPM) causes a pK lowering of 1.3 pK units (Table III).

From Dreiding models it seems likely that steric interactions will prevent the biphenylyl group from achieving coplanarity in the anion of *o*-BBP and probably interfere with the conjugation to the central carbon. The experimental result that *o*-BBP has essentially the same acidity as the unsubstituted DPM (ca. 1.7 pK units less acidic than *p*-BBP) suggests that this effect is just balanced by the inductive effect of the *o*-phenyl group.

Experimental Section

Melting points were determined on a Büchi apparatus and are not corrected. Visible spectra were measured on a Cary 118 spectrometer (20 nm/in.; 1 nm/s).

Procedure. The procedure for measuring the spectra of the cesium salts has been described in detail.[4] The equilibrium constants in Table II were determined using the previously reported procedures.[1,5] This table is arranged such that the more acidic hydrocarbon is given as R_1H in equilibrium 1, and K is always >1. Table III summarizes the results as pK values. These values actually relate to the equilibrium of each hydrocarbon in eq 1 with 9-phenylfluorene, with a pK of 18.49 assigned to the latter, and are given on a per hydrogen basis.

***o*- and *p*-Benzylbiphenyl.** A commercial sample of benzylbiphenyl (Eastman Organic Chemicals; a mixture of the ortho and para isomers) was initially purified by subliming out the biphenyl present as a contaminant [32–35 °C (1 mm)]. The residual mixture (150 mg) was cleanly separated by preparative thin-layer chromatography (TLC) on a 20 × 20 cm silica gel F-254 plate (Brinkman Co.) with cyclohexane as eluent to give (after recrystallization from 95% EtOH) 13 mg of biphenyl [R_f 0.95; mp 68–69 °C (lit.[6a] mp 69–70 °C)], 59 mg of *o*-benzylbiphenyl [R_f 0.83; mp 54–55 °C (lit.[6b] mp 54 °C)], and 22 mg of *p*-benzylbiphenyl [R_f 0.70; mp 83–84 °C (lit.[6b] mp 85 °C)].

Acknowledgment. This work was supported by NIH USPH Grant GM-12855.

Registry No.—*p*-BBP, 613-42-3; *o*-BBP, 606-97-3.

References and Notes

(1) (a) A. Streitwieser, Jr., E. Ciuffarin, and J. H. Hammons, *J. Am. Chem. Soc.*, **89,** 63 (1967). (b) A. Streitwieser, Jr., J. R. Murdoch, G. Häfelinger, and C. J. Chang, *ibid.*, **95, 4248** (1973). A summary is available for Japanese readers: A. Streitwieser, Jr., and L. L. Nebenzahl, *Yuki Gosei Kagaku Kyokai Shi,* **33,** 889 (1975).
(2) The pK of *p*-benzylbiphenyl in Me_2SO–MeOH has been reported by E.-C. Steiner and J. M. Gilbert, *J. Am. Chem. Soc.*, **87,** 382 (1965).
(3) Steric inhibition of resonance has been observed by Bowden and Stewart when comparing the effect of *o*- and *p*-nitro groups on the acidity of diphenylmethane: K. Bowden and R. Stewart, *Tetrahedron,* **21,** 261 (1965).
(4) G. Häfelinger and A. Streitwieser, Jr., *Chem. Ber.,* **101,** 672 (1968).
(5) A. Streitwieser, Jr., J. H. Hammons, E. Ciuffarin, and J. I. Brauman, *J. Am. Chem. Soc.*, **89,** 59 (1967).
(6) (a) W. H. Zartman and H. Adkins, *J. Am. Chem. Soc.*, **54,** 3398 (1932); (b) G. Goldschmiedt, *Monatsh. Chem.*, **2,** 432 (1881).

Synthesis of 2,6-Diacetonylpiperidine. X-ray Diffraction Analysis of Its *N*-Benzoyl Derivative[1]

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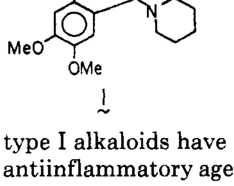
The 39 alkaloids which have been isolated from members of the *Lythraceae* plant family[2] may be classified according to three structural types. The type I alkaloids, quinolizidine lactones, are represented by cryogenine (**1**).[2a] The type II alkaloids, e.g., lythrancine I (**2**),[2b] are also quinolizidine alkaloids, but with a carbocyclic ring. Finally, the type III alkaloids are piperidine alkaloids, e.g., lythranidine (**3**).[2c] Some of the type I alkaloids have been investigated for use as sedatives, antiinflammatory agents, and as diuretics.[3] There have been no reports of pharmacological studies on the type II or III al-



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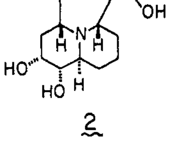

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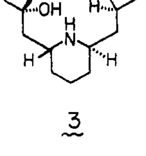

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