acid probably being an oxidation product of the initially formed nitro compound. Subsequent reactions showed that quantitative reaction could be achieved at 100° within 30 min and that 10% reaction was reached after 30 min at 80°. At these shorter times, β-nitrostyrene was the only reaction product found. Identification of β-nitrostyrene was made through comparison of spectra and melting points with an independently prepared sample.

1,1-Diphenyl-2-bromoethylene with Silver Nitrate.—Quantitative reaction was shown after 5 hr at 130°. The weight of crude product obtained represented quantitative conversion into 1,1-diphenyl-2-nitroethylene. The crude product was recrystallized from Skellysolve H to give yellow needles, mp 86–88° (lit.[14] mp 86–88°), which gave an nmr spectrum which was essentially identical with that of the crude product and as expected for the nitro olefin. Elemental analysis gave results expected for the nitro compound.

1-Bromo-2-phenylpropene with Silver Nitrate.—Complete reaction was reached after 2 hr at 130°. The crude product was initially purified by vacuum distillation [90–100° (0.5–0.75 mm)]. Final purification was achieved through chromatography on silica gel. The 2-phenyl-1-nitropropene was eluted with Skellysolve H. Minimum yield was 75%. The ir spectrum showed prominent peaks at 6.38, 6.61, and 7.46 μ;[15] mass spectrum *m/e* 163 (P, 9%), 129 (P − 34, 33%), 117 (P − 46, 36%), 116 (P − 47, 37%), 115 (P − 48, 100%), 91 (P − 72, 78%), 77 (P − 86, 73%).

Triphenylbromoethylene with Silver Nitrate.—Only a trace of silver bromide was seen after heating for 6 hr at 130°. Reaction work-up yielded only unreacted starting material.

Triphenyliodoethylene with Silver Nitrate.—After 24 hr at 130°, 80% reaction was reached. The crude product obtained in 75% yield was purified by chromatographing over silica gel. Triphenylnitroethylene was eluted with 20% benzene–Skellysolve H. Recrystallization from Skellysolve yielded yellow needles with mp 176–178° (lit.[16,17] mp 175–176°); mass spectrum *m/e* 301 (P − 48%), 255 (P − 46, 100%), 253 (P − 48, 33%), 178 (P − 123, 22%).

1-Bromo-2-methylpropene.—The reaction of this vinyl bromide with silver nitrate resulted in a rather violent explosion approximately 10 min after the sealed tube was immersed in the oil bath at 130°. The magnitude of the explosion appeared to be too large to be accounted for by simple increased vapor pressure of the solvent system. A preliminary run with small amounts (∼250 mg) of the halide gave no explosion and a silver bromide precipitate formed. The explosion occurred when larger amounts (3.0 g) of halide were used for product study.

Registry No.—Silver nitrate, 7761-88-8; 2-phenyl-1-nitropropene, 15795-70-7.

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[14] R. Anschutz and A. Hilbert, *Ber.*, **54**, 1854 (1921).

[15] J. F. Brown, Jr., *J. Amer. Chem. Soc.*, **77**, 6341 (1955).

[16] E. A. Shilov, *J. Russ. Phys. Chim. Soc.*, **62**, 95 (1930).

[17] L. Hellerman and R. Garner, *J. Amer. Chem. Soc.*, **57**, 139 (1935).

The Hydrogen-Bonding Basicity of Aryl Alkyl Ketones

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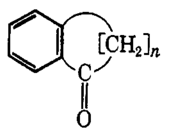
Received November 21, 1968

We wish to report the results of experiments which define systems for the study of conjugation effects on the hydrogen-bonding propensity of aryl alkyl ketones,[2,3] and to propose a tentative interpretation of these effects.

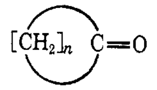
Bellamy and Pace[4] have observed that benzaldehyde and acetaldehyde appear to be hydrogen-bonding bases of comparable strength, and that acetone is a slightly better hydrogen-bonding base than acetophenone. From data pertaining to these and other compounds they were led to the conclusion that conjugation has little effect on the hydrogen-bonding propensity, and that it sometimes produces inexplicable disparities.[4]

It seemed to us that intuitively one would expect that resonance interaction with an aryl group would increase the hydrogen-bonding basicity of a carbonyl group, and we envisaged a system in which the extent of orbital overlap with an aryl group might be controlled without drastically changing the nature of the carbonyl group in other respects.

Hydrogen-bonding basicities were determined for a series of benzocyclanones (**1–4**) and for a corresponding series of cyclanones (**5–8**). The difference ($\Delta\nu_{OH}$) between the O—H stretching frequency of phenol alone in carbon tetrachloride and that of phenol in carbon tetrachloride containing a benzocyclanone or cyclanone was assumed to be proportional to the strength of the $C{=}O\cdots HOC_6H_5$ hydrogen bond.[3] The magnitude of the spectral shift was observed to decrease with increasing ring size in the benzocyclanone series, but increased with increasing ring size in the cyclanone series.[5] The data are summarized in Table I.



1, $n = 2$
2, $n = 3$
3, $n = 4$
4, $n = 5$



5, $n = 4$
6, $n = 5$
7, $n = 6$
8, $n = 7$

TABLE I

HYDROGEN-BONDING AND ULTRAVIOLET SPECTRAL DATA FOR BENZOCYCLANONES AND CYCLANONES

Benzocyclanone	$\Delta\nu_{OH}$, cm^{-1}	λ_{max}, cm$^{-1\,a}$	$\epsilon_{max}{}^{a}$	Cyclanone	$\Delta\nu_{OH}$, cm^{-1}
1	224	41,900	12,720	**5**	208
2	215	41,200	11,450	**6**	209
3	211	41,600	9,000	**7**	217
4	201	41,100	6,500	**8**	228

[a] See ref 10.

In an effort to rationalize the behavior of the benzocyclanones a working hypothesis concerning the factors that contribute most significantly to the hydrogen-bonding basicity was adopted. The relative basicity of a benzocyclanone was considered to be dependent upon (1) influences that are an intrinsic function of the ring size of the cyclanone portion, and (2) some factor which is a function of the degree of conjugation

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[1] To whom inquiries should be addressed.

[2] We have terminated research in this area and invite interested researchers to pursue a more complete investigation.

[3] There have been numerous studies of hydrogen bonding between ketones and phenols; yet for several reasons conclusions based on many such investigations must now be considered tentative. T. D. Epley and R. S. Drago [*J. Amer. Chem. Soc.*, **89**, 5770 (1967)] have published a succinct review of the problems involved.

[4] L. J. Bellamy and R. J. Pace, *Spectrochim. Acta*, **19**, 1831 (1963).

[5] The same trend for cyclanones has been observed by others[6] using CH_3OD as a hydrogen-bonding acid. Lactones and cyclic ethers were also studied. The reported trend for ethers[6] was not observed when measurements of ΔH for hydrogen-bond formation were made,[7] but the accuracy of similar enthalpy measurements has been questioned.[3]

[6] M. Tamres and S. Searles, Jr., *J. Amer. Chem. Soc.*, **81**, 2100 (1959).

[7] R. West, D. L. Powell, M. K. T. Lee, and L. S. Whatley, *ibid.*, **86**, 3227 (1964).

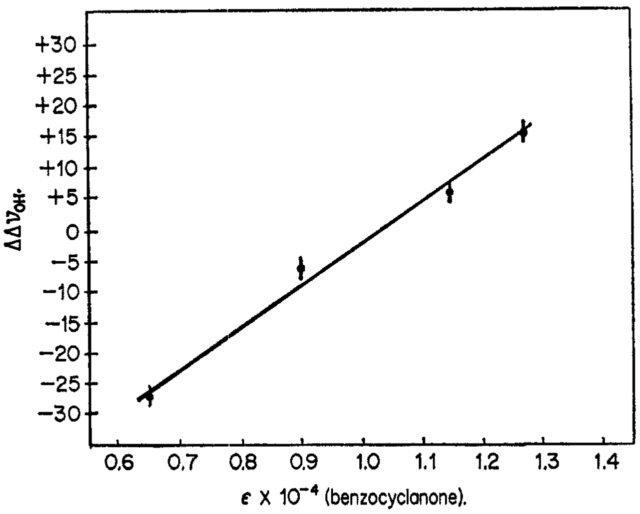

Figure 1.—A plot of the difference between the hydrogen-bonding propensity of a benzocyclanone and the corresponding cyclanone *vs.* the extinction coefficient of the intramolecular charge-transfer band of the benzocyclanone.

between the aryl and carbonyl moieties. The behavior of the cyclanones was assumed to reflect the ring-size effect. The $\Delta\nu_{OH}$ for each cyclanone was therefore subtracted from that for the corresponding benzocyclanone in an effort to correct for ring-size factors. The adjusted values ($\Delta\Delta\nu_{OH}$) were then examined to see if they could be correlated with the degree of conjugation in the benzocyclanones.

The molar absorptivity (ϵ) of the intramolecular charge-transfer band[8] of each benzocyclanone was taken as a measure of the extent of orbital overlap between the aromatic ring and the carbonyl group. The magnitude of ϵ is related to the average deviation of these groups from coplanarity.[9] For a benzocyclanone such as 1-indanone, effective overlap is reflected in the large value of ϵ, whereas in benzocyclooctanone overlap is diminished as a result of the conformational strain that would be associated with the coplanar conformation, and this diminution is reflected in a smaller ϵ (Table I).

Figure 1 is a plot of $\Delta\Delta\nu_{OH}$ *vs.* ϵ, and it is apparent that a good linear relationship exists.[13] This suggests that as the average interplanar angle of the carbonyl and aryl groups in a benzocyclanone increases, resonance interaction subsides and the influence of the electron-withdrawing inductive effect of the aryl group becomes evident.

This effect of aryl rotational conformation on H-bonding propensity does not seem to have been considered in previous studies. Although it is a relatively minor influence, it is obvious that it could contribute to the unexplained disparities noted by Bellamy.[4] Obviously, if one selected data for a particular benzocyclanone–cyclanone pair he could support opposite conclusions regarding the effect of the aryl group on $\Delta\nu_{OH}$.

We believe the conjugation effect also contributes to the hydrogen-bonding trends observed for certain other ketones. For example, Table II shows the decrease in $\Delta\nu_{OH}$ observed for phenol with two series of phenones. In both series the intrinsic steric and electronic effects of R as well as its influence on the coplanarity of the phenyl and carbonyl groups could affect the magnitude of the hydrogen-bonding shift. However, hydrogen-bonding shifts for a related series of ketones (Table III) in which the phenyl group has been replaced by methyl do not show so great a sensitivity to the nature of R. This may indicate that the decrease in $\Delta\nu_{OH}$ observed for the phenones as R increases in size is partially the result of the phenyl group being forced out of coplanarity with the carbonyl.

TABLE II

HYDROGEN-BONDING SHIFTS FOR PhCOR

R	Registry no.	$\Delta\nu_{OH}$, cm^{-1}
CH_3	98-86-2	194
CH_2CH_3	93-55-0	164
$CH(CH_3)_2$	611-70-1	166
$C(CH_3)_3$	938-16-9	150
CH_2Ph	451-40-1	138
$CH(Ph)_2$	1733-63-7	126
$C(Ph)_3$	466-37-5	109

TABLE III

HYDROGEN-BONDING SHIFTS FOR CH_3COR

R	Registry no.	$\Delta\nu_{OH}$, cm^{-1}
CH_3	67-64-1	202
CH_2CH_3	78-93-3	191
$CH(CH_3)_2$	563-80-4	188
$C(CH_3)_3$	75-97-8	188
$C(Ph)_3$	795-36-8	156

Experimental Section

Ketones.—All ketones used were either redistilled or recrystallized commercial products or were prepared by standard literature procedures. The purities of all except the trityl compounds were shown to be at least 99% as indicated by vapor phase chromatography. The trityl compounds melted over less than a 2° range and gave one spot when subjected to thin layer chromatography.

Infrared spectra were obtained on a Perkin-Elmer Model 421 grating spectrophotometer using 1-cm cells. Spectra of carbon tetrachloride solutions of phenol (0.01 *M*) plus a ketone (0.1 *M*) *vs.* a reference solution of the ketone (0.1 *M*) alone in carbon tetrachloride yielded ν_{OH} values with an estimated accuracy of ± 3 cm^{-1}.

Registry No.—**1**, 83-33-0; **2**, 529-34-0; **3**, 826-73-3; **4**, 829-14-1; **5**, 120-92-3; **6**, 108-94-1; **7**, 502-42-1; **8**, 502-49-8.

Acknowledgment.—Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

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(8) S. Nagakura and J. Tanaka, *J. Chem. Phys.*, **22**, 236 (1954); S. Nagakura, *ibid.*, **23**, 1441 (1955).

(9) Assuming a cosine-squared relationship, angles of twist between the plane of the carbonyl group and that of the aryl group have been calculated.[10,11] However, the justification for such calculations has been questioned.[12]

(10) G. D. Heddon and W. Brown, *J. Amer. Chem. Soc.*, **75**, 3744 (1953).

(11) E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).

(12) N. L. Allinger and E. S. Jones, *J. Org. Chem.*, **30**, 2165 (1965).

(13) A good linear relationship is also obtained if one plots $\Delta\nu_{OH}$ benzocyclanone *vs.* ϵ, and this result suggests identical conclusions. The linear relationship observed between $\Delta\Delta\nu_{OH}$ and ϵ does not necessarily confirm that the same ring size influences are operative in both cyclanones and benzocyclanones.