1108. *The Ethynyl–Hydrogen Bond. Part II.* The Association of Benzoylacetylene with Aromatic Hydrocarbons and with n-Butyl Ether studied by Infrared and Proton Resonance Spectroscopy and by Calorimetry.*

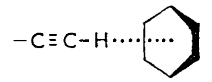
By J. C. D. BRAND, G. EGLINTON, and J. TYRRELL

Association of benzoylacetylene with benzene, toluene, *p*-xylene, and mesitylene has been studied over a range of temperatures. Association constants for the system benzoylacetylene–benzene and benzoylacetylene–toluene were determined both from the infrared and proton spectra, the results being in moderately good agreement. Enthalpies of association were estimated from the temperature-dependence of the association constants, and from calorimetric measurements. The results, which do not cohere very well, indicate that ΔH lies in the range -5 to -6 kcal./mole. Parallel measurements are reported for the association of benzoylacetylene with n-butyl ether.

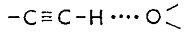
THE hydrogen-bonded association of benzoylacetylene (I) with benzene, toluene, *p*-xylene, and mesitylene has been studied by infrared spectroscopy, proton resonance, and calorimetry; and a more conventional type of association, with n-butyl ether, has been followed simultaneously for comparison. In both systems the results are analysed on the assumption that no complex is formed other than 1 : 1 complexes. The complex with benzene is presumed to have the structure (II), analogous to the complexes of halogenoforms with benzene,[1] though there are inconsistencies in the results which may indicate that other forms are present also. The complex with butyl ether resembles that formed with ethyl ether (Part I) and is thought to have the structure (III). Benzoylacetylene was chosen because its acidity is high relative to that of other acetylenes.[2-6]

Ph·CO·C:CH

(I)



(II)



(III)

Infrared Measurements.—The method was similar to that described in Part I, *i.e.*, the integrated intensity associated with the ≡C–H stretching mode was measured in a series of binary mixtures of " active " solvent and cyclohexane. Representative spectra in mesitylene–cyclohexane and n-butyl ether–cyclohexane are shown in Figure 1. The sharp peak near 3305 cm.$^{-1}$ is attributed to unassociated benzoylacetylene, the broad band at lower frequency to the complex. In this system of acetylenic compound (A) and " active " solvent (B) in equilibrium with the 1 : 1 complex (AB) in presence of an inert solvent, the (mole fraction) equilibrium constant is given by

$$K_N = \frac{m_{\mathrm{AB}}}{m_{\mathrm{A}}x_{\mathrm{B}}} \qquad (1)$$

in which m stands for molality and x for mole fraction. Since the absorption bands of A and AB overlap one another the integrated absorption intensity A of the fused bands

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* Part I, J. C. D. Brand, G. Eglinton, and J. F. Morman, *J.*, 1960, 2526.

[1] C. J. Creswell and A. L. Allred, *J. Phys. Chem.*, 1962, **66**, 1469; *J. Amer. Chem. Soc.*, 1963, **85**, 1723; A. Allerhand and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1963, **85**, 1715.

[2] B. Wojtkowiak and R. Romanet, *Compt. rend.*, 1960, **250**, 3980.

[3] R. West and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1961, **83**, 765.

[4] N. Nakagawa and S. Fujiwara, *Bull. Chem. Soc. Japan*, 1960, **33**, 1634.

[5] E. A. Gastilovich, D. N. Shigorin, E. P. Gracheva, I. A. Chekula, and M. F. Shostakovskii, *Optika y Spectroskopiya*, 1961, **10**, 312.

[6] J. V. Hatton and R. E. Richards, *Trans. Faraday Soc.*, 1961, **57**, 28.

was measured in the range 3100—3400 cm.$^{-1}$ and its dependence on x_B analysed by means of the equation

$$x_B(A - A_A)^{-1} = x_B(A_{AB} - A_A)^{-1} + K_N(A_{AB} - A_A)^{-1} \qquad (2)$$

Here, A_A and A_{AB} are the integrated intensities associated with the free and H-bonded benzoylacetylene, and A is the intensity recorded for the unresolved absorption of both forms in a mixed solvent. A_A can be determined in cyclohexane solution, and K_N and A_{AB} are then obtained from a plot of $x_B(A - A_A)^{-1}$ against x_B. The benzoylacetylene concentration in these experiments was 0·05M, while x_B was varied in the range 0·1—1·0 mole fraction. The assumption underlying this analysis is that A_A and A_{AB} are unchanged in cyclohexane, benzene (or other active solvent), and their mixtures.

To obtain ΔH, the measurements above were carried out near room temperature and in cells heated to 50 and 70°. It could be confirmed that A_A did not change significantly with temperature; but there is no means of testing experimentally that A_{AB} is also constant, and this must be assumed.

TABLE 1

Infrared intensity data for ν(CH) at 27° for benzoylacetylene in n-butyl ether–cyclohexane

x_B	0·0	0·1	0·2	0·3	0·4	0·5	0·6	0·7	0·8	0·9	1·0
A (M^{-1} cm.$^{-2}$)	6140	7470	8320	9330	9960	10,320	10,610	10,910	11,520	11,470	11,810
$10^4 x_B (A - A_A)^{-1}$	—	0·75	0·92	0·94	1·05	1·19	1·34	1·47	1·49	1·69	1·76

TABLE 2

K_N and ΔH from infrared measurements

H-donor	Solvent: Cyclohexane–	K_N (25°)	Association (%) ($x_B = 1$)	A_{AB} (M^{-1} cm.$^{-2}$)	ΔH (kcal./mole)
Ph·CO·C⋮CH	Benzene	$0{\cdot}6_1$	38	13,600	$-3{\cdot}_9$
	Toluene	1·4	58	10,900	$-5{\cdot}_4$
	p-Xylene	2·4	71	10,300	$-5{\cdot}_9$
	Mesitylene	3·0	75	9600	—
	n-Butyl ether	1·8	64	15,000	$-6{\cdot}_4$
Ph·C⋮CH	n-Butyl ether	$0{\cdot}7_6$	43	14,500	—

The results are summarised in Tables 1 and 2. Table 1 gives representative data for the benzoylacetylene–butyl ether–cyclohexane system. Table 2 summarises the results for the five systems studied using benzoylacetylene as H-donor, and for one system utilising phenylacetylene. The equilibrium constants given in Part I for benzoylacetylene (K_N = 2·0) and phenylacetylene (K_N = 1·1) in ethyl ether–carbon tetrachloride agree satisfactorily with the present series. Errors in K_N and ΔH are not necessarily random so that the

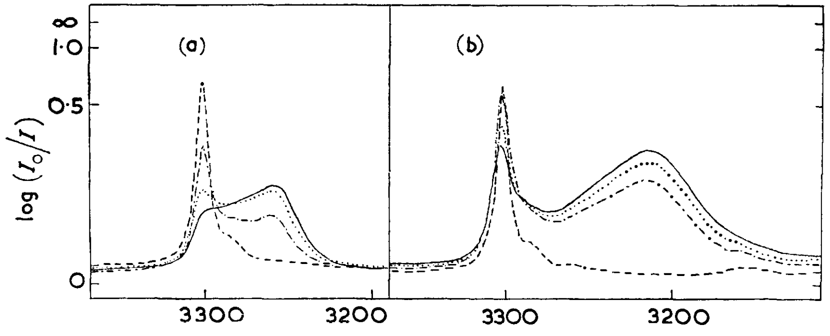

FIGURE 1.—Ph·CO·C⋮CH, (*a*) 0·05M in mesitylene–cyclohexane (0·5 mm. cell). x_B = 0, – – – –; x_B = 0·3, — · — · —; x_B = 0·7, · · · ·; x_B = 1·0, ——. (*b*) 0·05M in butyl ether–cyclohexane (0·5 mm. cell). x_B = 0, – – – –; x_B = 0·4, — · — · —; x_B = 0·7, · · · ·; x_B = 1·0, ——. Cell well temp., 27°.

least-squares treatment used to obtain the quantities in Table 2 probably gives optimistic estimates of error. We judge that the K's are reliable to about $\pm 25\%$, and ΔH to about ± 1 kcal./mole.

Proton Resonance.—In these experiments the relative shift of the ethynyl proton in the mixed solvents was measured by using the cyclohexane resonance as internal standard. Aromatic solvents produced the expected upfield shift,[6,7] whereas butyl ether displaced the signal towards lower field. Neglecting for the moment the effects of solvent anisotropy, the shifts can be analysed by an equation similar to equation (2), namely

$$x_B\delta^{-1} = x_B\delta_{AB}^{-1} + (K_N\delta_{AB})^{-1} \qquad (3)$$

in which δ is the observed shift of the ethynyl proton in the binary solvent and δ_{AB} is the shift (not observable) due to the complex, both relative to the position of the "free" ethynyl resonance (observable in pure cyclohexane) which is arbitrarily assigned a shift of zero. As it stands, this equation can probably be applied to the butyl ether–cyclohexane system; but not to systems that involve aromatic hydrocarbons, since the large anisotropy associated with benzene and its derivatives produces an upfield displacement which is not taken into account.[7,8] From the very few molecules studied that do not associate with benzene, this shift amounts to about 0·4 p.p.m. and is roughly the same whether the molecule is rod- or disc-like.[1,8-10] We may consider, therefore, that the "free" benzoylacetylene and cyclohexane signals both move upfield as benzene replaces cyclohexane, maintaining about the same shift relative to one another: though it seems unlikely that this displacement is maintained for associated benzoylacetylene, since the benzene molecule in the complex then excludes other solvent molecules from the space in which they are most effective as anisotropic neighbours. So, in considering the complex, we expect it will be influenced by the anisotropy of relatively distant benzene molecules only and we estimate their contribution as about one-fifth that experienced by protons which are not complexed in any way with the solvent. In consequence, we write

$$\delta = \delta_0 + 0{\cdot}8\delta_1 x_B \qquad (4)$$

(where $\delta_1 = 0{\cdot}43$ p.p.m.) in which δ_0 is the observed shift of the ethynyl proton in the binary solvent relative to the reference signal (the "free" ethynyl proton in cyclohexane); and δ_1 is the shift observed (against an external reference) for cyclohexane when this substance is measured first in the liquid state and then in dilute solution in benzene.[10] In order to analyse the results, instead of the observed shift we substitute δ (equation 4) into equation (3). Anisotropy appears much less important for solutions in butyl ether and has been neglected (equivalent to putting $\delta_1 = 0$ in equation 4).

The analysis of results for benzoylacetylene in benzene–cyclohexane is shown in Figure 2. The points show scatter but no other non-linear trend and yield K_N (25°) $= 0{\cdot}7_1$, $\delta_{AB} = +2{\cdot}2_2$ p.p.m. K_N agrees satisfactorily with the value in Table 2. (It is worth noting that the assumption $\delta_1 = 0$, effectively ignoring the solvent anisotropy, also gives a linear plot from which one obtains $K_N = 1{\cdot}1$, $\delta_{AB} = +1{\cdot}1_2$ p.p.m.: K_N is therefore quite sensitive to δ_1, which is unfortunate since we know too little about this quantity.) δ_{AB} is of interest n that it gives some insight into the structure of the complex. According to the iso-shielding diagram given by Johnson and Bovey,[11] a paramagnetic shift of 2·2 p.p.m. indicates that the H-bonded proton is about 2·7 Å from the plane of the ring, assuming that it lies on the six-fold axis. The sum of van der Waals contact distances is about

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[7] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, 1959, ch. 16.

[8] W. G. Schneider, *J. Phys. Chem.*, 1962, **66**, 2653.

[9] A. D. Buckingham, T. Schaefer, and W. G. Schneider, *J. Chem. Phys.*, 1960, **32**, 1227.

[10] R. J. Abrahams, *Mol. Phys.*, 1961, **4**, 369.

[11] C. E. Johnson and F. A. Bovey, *J. Chem. Phys.*, 1958, **29**, 1012.

2·9 Å,[12] so that the ring–proton separation appears slightly less than the contact distance. This receives support from the crystal structure of derivatives of benzoylacetylene where the O ··· C distance between neighbours indicates an H-bond distance, O ··· H, of 2·2 Å, roughly 0·4 Å less than the contact value.[13] (The shift obtained on the assumption that $\delta_1 = 0$, namely $\delta_{AB} = 1{\cdot}1$, corresponds to a ring–proton distance of about 3·6 Å, which seems physically unreasonable.)

If we maintain the assumption that $\delta_1 = 0{\cdot}43$ p.p.m., similar results follow for the toluene–cyclohexane system, except for some reduction in δ_{AB} which may be the result of deshielding by the methyl group. With *p*-xylene and mesitylene, however, the plots analogous to that in Figure 2 are non-linear and no satisfactory analysis is possible.

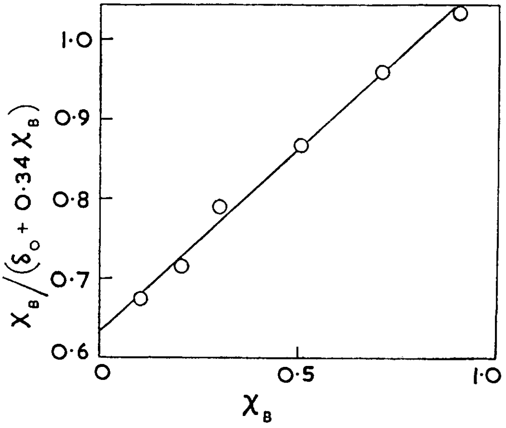

FIGURE 2. Equilibrium at 25° in the system Ph·CO·C⋮CH + C_6H_6

Linearity can be restored by taking $\delta_1 = 0{\cdot}2$ p.p.m., or even $\delta_1 = 0$, but to do this is altogether too arbitrary. For this reason the summary of results (Table 3) contains data for benzene, toluene, and *n*-butyl ether solutions only.

TABLE 3

K_N and ΔH from proton resonance

H-donor	Solvent: Cyclohexane–	K_N (25°)	Association (%) ($x_B = 1$)	δ_{AB} (p.p.m.)	ΔH (kcal./mole)
Ph·CO·C⋮CH	Benzene	$0{\cdot}7_1$	41	+2·22	$-1{\cdot}_8$
	Toluene	1·1	52	+1·65	$-2{\cdot}_1$
	n-Butyl ether	2·1	68	−1·04	$-3{\cdot}_7$

The measurements in these three systems were repeated at different temperatures and values of ΔH calculated from the temperature variation of K_N. Given the considerable uncertainty in the K's, and the even greater uncertainty in their temperature-coefficients, ΔH for the benzoylacetylene–butyl ether system is in acceptable agreement with the value obtained from the infrared measurements. The toluene system, which was examined in the range 6—50°, gave internally consistent results (*e.g.*, constant δ_{AB}) which, however, corresponded to a very low value for the heat of association, $\Delta H = -2$ kcal./mole. In view of the uncertainty clouding the interpretation in the aromatic solvents this result should not be accorded much weight.

Calorimetry.—The heat of solution, L_2, of benzoylacetylene in the various solvents was measured directly. Since heat is absorbed, the values of L_2 (the integral heat per mole of benzoylacetylene dissolved) so determined are positive in sign.

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[12] L. Pauling, " The Nature of the Chemical Bond," 3rd edn., Cornell University Press, New York, 1960, ch. 7.

[13] G. Ferguson and J. Tyrrell, *Chem. Comm.*, 1965, **10**, 195.

X-Ray studies have shown[13] that single crystals of the 2-bromo- and 2-chloro-derivatives of benzoylacetylene possess zig-zag arrangements of intermolecular $\equiv C{-}H \cdots O{=}C$ hydrogen bonds, there being an average of one such bond per molecule in the crystal. When such a crystal dissolves in an inert solvent, then the breaking of these bonds should provide the major contribution to the heat of solution. *X*-Ray data are not available for benzoylacetylene but the infrared shifts $[\Delta\nu = \nu_{\text{solvent}} - \nu_{\text{solid}}]$ are approximately the same, 80 cm.$^{-1}$ for $\nu(\equiv CH)$ and 30 cm.$^{-1}$ for $\nu(CO)$, in benzoylacetylene and its 2-bromo-derivative. The molar heat of solution of benzoylacetylene in cyclohexane was found to be +7·41 kcal./mole, constant in the range 0·01—0·005M where the infrared spectrum shows no self-association, so that we identify this with the limiting value. Apart from the H-bond contribution, the heat change in forming the solution would be small, probably a few hundred cal./mole at most; thus the heat of rupture of the $\equiv C{-}H \cdots O{=}$ bonds must be in the neighbourhood of +7·0—7·5 kcal./mole, a surpisingly high value.

When benzoylacetylene dissolves in benzene or other "active" solvent, the heat of solution contains a contribution from the formation of H-bonds to the solvent. The heat of solution is smaller than in cyclohexane, since the heat absorbed in rupturing the crystal H-bonds is in part returned through association with the solvent. The several values of L_2 are collected in Table 4. For the simple model used here, [L_2 (benzene) — L_2 (cyclohexane)] represents the heat evolved in forming $m_{AB}/(m_A + m_{AB})$ moles of complex. In taking differences, minor contributions to L_2 from sources other than the formation or rupture of H-bonds, will tend to cancel.

TABLE 4

Integral heats of solution of benzoylacetylene

Solvent	L_2 (kcal./mole)	$L_2 - L_2(C_6H_{12})$ (kcal./mole)	Solvent	L_2 (kcal./mole)	$L_2 - L_2(C_6H_{12})$ (kcal./mole)
Cyclohexane	7·41	—	*p*-Xylene	4·87	−2·54
Benzene	4·49	−2·92	Mesitylene	4·72	−2·69
Toluene	4·78	−2·63	n-Butyl ether ...	4·53	−2·88

DISCUSSION

We first examine how the different measurements fit together. For benzoylacetylene in butyl ether–cyclohexane $K_N = 2{\cdot}0$ ($\pm 0{\cdot}7$) and the fraction of molecules complexed in the pure ether is about $0{\cdot}6_7$. The mean of two measured values of ΔH is -5 kcal./mole, thus the contribution to L_2 is $-3{\cdot}_3$ kcal./mole which checks satisfactorily with $L_2(Bu_2O) - L_2(C_6H_{12}) = -2{\cdot}9$ kcal./mole. In the toluene–cyclohexane system, disregarding the value of ΔH indicated by proton resonance, we have $\Delta H = -5{\cdot}_4$ and $m_{AB}/(m_A + m_{AB}) = 0{\cdot}5_8$; thus the contribution to L_2 is $-3{\cdot}_1$ kcal., also in moderately good agreement with the calorimetric value. For the benzene and *p*-xylene systems, on the other hand, agreement is rather poor and the discrepancies are in opposite directions. At most, it can be said that ΔH for the π-complexes is probably in the range -5 to -6 kcal./mole, roughly equal to ΔH for the butyl ether complex but substantially smaller than the value about -7 kcal./mole indicated for self-association to the carbonyl group. From benzene to mesitylene there appears to be a definite trend towards increased association, presumably because the alkyl groups donate electrons to the ring and so enhance its capacity to act as proton-acceptor. The trend is also regular, that is, there is little evidence for steric crowding as the number of ring methyl groups is increased. The values of ΔH are substantially higher than those recorded for the association of chloroform with benzene[1] and ethers (refs. 1, 14, and Part I).

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[14] B. B. Howard, C. F. Jumper, and M. T. Emerson, *J. Mol. Spectroscopy*, 1963, **10**, 117.

The failure to obtain more consistent results by different methods is disappointing. We have been impressed by the fact that the butyl ether system is in this respect better-behaved than the aromatic systems; for the paremeters are so similar that it seems unlikely that the difference could be experimental. A possible reason may be that the π-complexes are of mixed type; some of the form (II), and some of a form preferred by Hatton and Richards [6,15] in which the benzoylacetylene lies in a plane parallel to that of the aromatic ring. The second type of complex may involve association through the carbonyl group of benzoylacetylene rather than the ethynyl group.[14] We consider that the infrared curves in Figure 1 require that complexes of the type (II) must be present, but not so as to exclude other forms of association. If so, an analysis based on the formation of a single type of 1 : 1-complex breaks down to some extent, partly because the different methods may discriminate between the modes of association. It is difficult to see otherwise why the proton spectra for *p*-xylene– and mesitylene–cyclohexane cannot be interpreted satisfactorily. Analysis of this relatively complex situation is outside the scope of this Paper.

EXPERIMENTAL

Infrared and Proton Spectra.—Infrared spectra were recorded with a Unicam S.P. 100 prism-grating spectrophotometer operated in the 3100—3400 cm.$^{-1}$ region with a spectral slit width of about 2 cm.$^{-1}$. Integrated intensities $A(\text{M}^{-1}\ \text{cm.}^{-2}) = (cl)^{-1}\int_{\text{band}} \ln(I^\circ/I)\,\text{d}\nu$ were reproducible to about $\pm 2\%$. The proton spectra were measured with an AEI RS2 spectrometer (60 Mc./sec.) fitted with a variable-temperature probe. Most measurements were carried out with 0·1M of benzoylacetylene solution. Results at 0·2 and 0·05M indicated that the extrapolation to infinite dilution could be neglected.

Calorimetry.—The calorimeter was a 0·5 l. Dewar vessel fitted with heater coil, Vibromixer stirrer, and Beckmann thermometer. The stirrer was run for about 30 min. while the calorimeter and its contents reached a steady state, temperatures being recorded at 30-sec. intervals; the benzoylacetylene was then brought into contact with the solvent by breaking a thin glass bulb and the temperature change recorded in the usual way. After a few minutes the system was calibrated by passing a current through the heater, the potential difference across the terminals being measured with a potentiometer. In control experiments, the heat of solution of 1 mole of potassium chloride in 160 moles of water was found to be 4·18 kcal., (lit.,[16] 4·18).

The data in Table 4 are calculated from the heat change observed on adding 0·01—0·005 moles of benzoylacetylene to 400 ml. of solvent. In this range concentration had no detectable effect, as shown by the results below:

Solvent	Moles of benzoyl-acetylene added	L_2 (kcal./mole)	Solvent	Moles of benzoyl-acetylene added	L_2 (kcal./mole)
C_6H_{12}	0·100	+7·40	C_6H_6	0·0100	+4·55
	0·0075	+7·42		0·0075	+4·44
	0·0050	+7·40		0·0050	+4·48

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[15] J. V. Hatton and R. E. Richards, *Mol. Phys.*, 1962, **5**, 153.

[16] R. A. Care and L. A. K. Staveley, *J.*, 1956, 4571; T. Davies, S. S. Singer, and L. A. K. Staveley, *J.*, 1954, 2304.