Stable Crystalline Complexes of Diphenylcyclopropenone with Substituted Acetic Acids[1]

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(Received August 16, 1973)

Diphenylcyclopropenone (DCP) forms 1:1 stable crystalline complexes with dichloroacetic acid, phenylacetic acid, diphenylacetic acid, trichloroacetic acid and cyanoacetic acid. The physical properties of these complexes are consistent with a hydrogen-bonded complexation between the carbonyl oxygen of DCP and the acidic hydrogen of the substituted acetic acid.

Diphenylcyclopropenone (DCP) (I) has been shown to form stable solid complexes with Lewis acids (BF_3, $SbCl_5$),[2] water,[3] and acetylenic dialcohols;[3] with methanol, a complex was formed in solution.[4] We wish to report that DCP forms 1:1 stable crystalline complexes with substituted acetic acids. The physical properties of these complexes are consistent with a hydrogen-bonded complexation between the carbonyl oxygen of DCP and the acidic hydrogen of the substituted acetic acid.

Treatment of DCP with an equimolar quantity of dichloroacetic acid (II) in boiling cyclohexane solution afforded a crystalline adduct of DCP and (II), mp 88—89 °C, in 78% yield, which analyzed for $C_{17}H_{12}Cl_2O_3$. The properties of this adduct (III) indicated that it was a 1:1 complex of DCP and II. In the solid state, the infrared molecular bands of DCP (II)[5] were shifted to lower frequencies: (KBr) 1850 cm^{-1} (I)→1820 cm^{-1} (III); 1630 cm^{-1} (I)→1595 cm^{-1} (III). (Similar shifts were observed in nujol.) The NMR spectrum of the complex III in $CDCl_3$ solution (100 MHz, δ=7.59 (m, 6H, *meta*+*para*) and 7.98 ppm (m, 4H, *ortho*)) showed a downfield shift of the aromatic protons relative to the respective absorptions of DCP.[6] It is noteworthy that the extent of the shift of the *ortho* protons (8 Hz) was identical to that of the *meta*+*para* protons. Thus, these shifts cannot be rationalized as due to a greater contribution of the "aromatic" dipolar structure of the cyclopropenium type in the complex (III). The longest wavelength maximum in the UV spectrum of I in cyclohexane solution, at 362 nm (ε=960), was absent in the corresponding spectrum of the complex (III). Instead, only a tailing towards the visible was observed. It has previously been suggested, on the basis of the wavelength, the relatively low extinction and the response to solvent, that the 362 nm band was due to intramolecular charge transfer of the "aromatic" 1,2-diphenylcyclopropenium oxide type.[4] The behaviour of this band in the UV spectrum of the complex is consistent with this interpretation.

Most revealing is the mass spectrum of the complex (III). It is not simply a superposition of the mass spectra of DCP and dichloroacetic acid (II). Certain of its features originate from the complex. Whilst the molecular ion ($[C_{17}H_{12}{}^{35}Cl_2O_3]^{+\cdot}$, *m/e* 334) was absent, the mass spectrum contained a most intense signal at *m/e* 207 (36% relative to that of *m/e* 206 $[DCP]^{+\cdot}$). It is most probably due to the 3-hydroxy-1, 2-diphenylcyclopropenium ion (IV). Thus, the mass spectrum strongly supports the proposed structure of the complex (III).

It appears that the chlorine substituents in the acetic acid moiety are not a prerequistite for the complexation. The formation of such a 1:1 complex between DCP and a substituted acetic acid proved to be a general reaction (at least for acetic acids with $pK_a < 4.3$). DCP reacts with phenylacetic acid, diphenylacetic acid, trichloroacetic acid, and cyanoacetic acid, in boiling cyclohexane solution to form, in each case, a 1:1 complex (see experimental section). The physical properties of these complexes closely resemble those of (III). The mass spectrum of each complex contained the prominent signal at *m/e* 207 representing the 3-hydroxy-1,2-diphenylcyclopropenium ion (IV). It should be noted that in solution, the complexation

TABLE 1. THE IR SPECTRA OF DCP–SUBSTITUTED ACETIC ACID COMPLEXES (2000—1500 cm^{-1} region)

Compound	Medium	ν (cm^{-1})		
DCP–$PhCH_2CO_2H$	Nujol	1870(m),	1845(s),	1825(s),
		1810(s),	1710(vs),	1595(vs),
		1580(vs),	1570(s)	
	KBr	1880_{sh}(m),	1860_{sh}(s),	1850(s),
		1835(s),	1820(s),	1775(w),
		1720(vs),	1605(vs),	1590(vs),
		1575(s)		
DCP–Ph_2CHCO_2H	Nujol	1875(m),	1845(s),	1830(s),
		1815(s),	1750(m),	1710(vs),
		1600(vs),	1585(vs),	1570(s)
	KBr	1890(w),	1860(s),	1845(s),
		1825(s),	1785(w),	1720(vs),
		1610(vs),	1595(vs),	1580(s)
DCP–Cl_2CHCO_2H	Nujol	1880(w),	1865_{sh}(s),	1850(s),
		1820(s),	1730(s),	1600(vs),
		1580(s),	1570(s)	
	KBr	1880(w),	1850(s),	1820(vs),
		1745(vs),	1620(m),	1595(vs),
		1575(vs),	1560(vs)	
DCP–Cl_3CCO_2H	Nujol	1845_{sh}(m),	1820_{sh}(s),	1795(vs),
		1700_{sh}(s),	1675(s),	1600(vs),
		1570(s)		
	KBr	1850(s),	1810(s),	1745(m),
		1600(vs),	1580(s),	1565(s)
DCP–$NCCH_2CO_2H$	Nujol	1875(w),	1850(m),	1815(vs),
		1750(m),	1720(vs),	1600(vs),
		1580(vs),	1570(vs)	
	KBr	1850(s),	1820(s),	1755(m),
		1720(vs),	1600(vs),	1585(vs),
		1575(vs)		

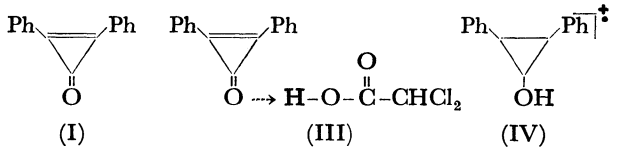
TABLE 2. THE NMR SPECTRA OF DCP-SUBSTITUTED ACETIC ACID COMPLEXES (in ppm)

Compound	δ (COOH)	δ (*ortho*[a])	δ (*meta*+*para*[a])	δ (Phenyl)	δ (CH)	δ (CH_2)	Δ
DCP		7.90	7.51				0.39
DCP-$PhCH_2COOH$	10.84	7.89	7.50	7.26		3.62	0.39
DCP-$Ph_2CHCOOH$	11.16	7.92	7.50	7.28	5.06		0.42
DCP-$Cl_2CHCOOH$	13.38	7.98	7.59		6.04		0.39
DCP-Cl_3CCOOH	14.56	7.98	7.59				0.39
DCP-$NCCH_2COOH$	12.72	7.94	7.57			3.55	0.37

a) (*ortho*) and (*meta*+*para*) refers to the chemical shifts of the center of the corresponding multiplets of the AB_2C_2 systems of the DCP residue.

could be effected directly by dissolving equimolar quantities of DCP and the substituted acetic acid in the appropriate solvent. Under such conditions, both the NMR spectra and the UV spectra were identical with those obtained from the respective solutions of crystalline complexes.

It is plausible to assume that the complexation involves a hydrogen bond between the oxygen of the polar carbonyl group of DCP and the acidic hydrogen of the substituted acetic acid. The shift to lower frequencies of the cyclopropenone bands in the infrared spectra in the solid state supports this hypothesis. Likewise, the strong signal in the mass spectra of the complexes at *m/e* 207 is consistent with the proposed structure. In solution (CH_2Cl_2), however, the infrared spectrum was, in each case, a superposition of the respective spectra of the two components. The exact structure of the complexes of DCP with the substituted acetic acids must await an X-ray-crystallographic determination.



(I) (III) (IV)

Cl_2CHCO_2H

(II)

Experimental

Melting points were taken on a Unimelt Thomas and Hoover capillary mp apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 457 Spectrophotometer. UV spectra were recorded on a Unicam SP 800 spectrophotometer. NMR spectra were recorded at 100 MHz on a Varian HA-100 spectrometer in $CDCl_3$ solutions. ^1H chemical shifts are reported in parts per million, downfield from Me_4Si. Mass spectra were recorded on a Varian MAT-311 spectrometer operating at 70 eV.

The Reaction of DCP (I) with Dichloroacetic Acid (II). DCP (0.515 g, 2.5 mmol)[7] and dichloroacetic acid (0.32 g, 2.5 mmol) were dissolved in 50 ml of boiling cyclohexane; the solution was refluxed for 15 min and gradually cooled to room temperature. The complex (III) crystallized from the solution. It was obtained as colourless crystals, mp 88—89 °C (cyclohexane) (78% yield). Found: C, 61.13; H, 3.38; Cl, 21.20%. Calcd for $C_{17}H_{12}Cl_2O_3$: C, 60.92; H, 3.61; Cl, 21.15%. ν_{max} (KBr) 3050 (w), 3000 (w), 2895 (w), 2845 (w), 2450 (w), 1880(w), 1850 (s), 1820 (vs), 1745 (vs), 1620 (m), 1595 (vs), 1575 (s), 1560 (s), 1480 (w), 1450 (s), 1370 (vs), 1290 (s), 1210 (m), 1175 (s), 1000 (w), 925 (w), 810 (s), 790 (w), 767 (vs), 687 (s), 590 (m), 520 (m), 473 (m), and 440 (m) cm^{-1}. λ_{max} (C_6H_{12}) 218, 222, 237_{sh}, 249_{sh}, 253_{sh}, 266, 274, 280, 289, 298, and 314_{sh} nm (ε 18900, 17900, 7200, 8200, 9300, 17100, 19600, 25600, 20400, 24000, and 4600); λ_{max} (CH_3CN) 219, 226, 230_{sh}, 265_{sh}, 280, 288, 296, 310_{sh}, and 330 nm (ε 18800, 16900, 14400, 13000, 24000, 24400, 28000, 13500, and 1820).

The following complexes were prepared in a similar manner:

DCP-Phenylacetic Acid Complex. Mp 76—77 °C, 75% yield. Found: C, 80.73; H, 5.18%. Calcd for $C_{23}H_{18}O_3$: C, 80.68; H, 5.30%. λ_{max} (C_6H_{12}) 217_{sh}, 222_{sh}, 227_{sh}, 249_{sh}, 267, 274_{sh}, 281, 289, 298, 314_{sh} and 356 nm (ε 23500, 20500, 15200, 6700, 15000, 18000, 22200, 19800, 22400, 7400, and 880).

DCP-Diphenylacetic Acid Complex. Mp 89—90 °C, 50% yield. Found: C, 83.56; H, 5.37%. Calcd for $C_{29}H_{20}O_3$: C, 83.23; H, 5.30%. λ_{max} (C_6H_{12}) 216_{sh}, 222_{sh}, 237, 249_{sh}, 266, 274, 281, 289, 298, 314_{sh}, and 344 nm (ε 36000, 28000, 9200, 10200, 19700, 21500, 27800, 19600, 24000, 1040, and 460).

DCP-Trichloroacetic Acid Complex. Mp 83—83.5 °C, 72% yield. Found: C, 55.33; H, 3.14; Cl, 28.43%. Calcd for $C_{17}H_{11}Cl_3O_3$: C, 55.24; H, 3.00; Cl, 28.77%. λ_{max} (C_6H_{12}) 219, 222, 227_{sh}, 266, 274, 281, 289, 298, and 314_{sh} nm (ε 18600, 18200, 14600, 14500, 17800, 21200, 18800, 22000, and 770).

DCP-Cyanoacetic Acid Complex. Mp 86—86.5 °C, 48% yield. Found: C, 73.94; H, 4.58; N, 5.03%. Calcd for $C_{18}H_{13}NO_3$: C, 74.22; H, 4.50; N, 4.89%. λ_{max} (C_6H_{12}) 221, 228, 290, 301, 314_{sh}, and 352_{sh} nm (ε 11500, 10900, 14100, 8200, and 440). For the preparation of this complex, a cyclohexane–benzene (50: 1) solution was employed.

The IR and the NMR spectra of the complexes are given in Tables 1 and 2.

We are deeply grateful to Professor Ernst David Bergmann of the Hebrew Universtiy of Jerusalem for his encouragement and his interest.

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