Hydrogen Bonding of Cyclopentadithiophenones and Fluorenone in Trifluoroacetic Acid. A Study of the Electronic Absorption, ^{1}H, and ^{13}C Nuclear Magnetic Resonance Spectra

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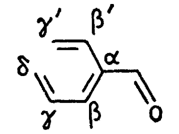
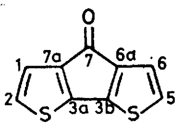
The electronic absorption bands of cyclopentadithiophenones and fluorenone show large shifts towards longer wavelengths when the solvent is changed from cyclohexane to CF_3CO_2H. ^{1}H and ^{13}C n.m.r. spectra of these ketones in $CDCl_3$ and CF_3CO_2H differ considerably. These observations point to strong hydrogen bond formation between the carbonyl oxygen atom and the solvent. Taking hydrogen bond formation into account by changing the core parameters of the oxygen atom, PPP calculations satisfactorily predict the bathochromic shifts of the electronic absorption bands. The calculated change in electron density at a particular carbon atom correlates well with the change in ^{1}H and ^{13}C n.m.r. chemical shifts as measured in $CDCl_3$ and CF_3CO_2H.

WE have previously found[1] that fluorenone (VII) and cyclopentadithiophenones (I)—(VI) are protonated at the ring system and/or at the carbonyl oxygen atom in the strong acidic system FSO_3H–SbF_5–SO_2 at -60 °C. From the ^{1}H n.m.r. spectra it was concluded that protonation of the carbonyl group did not drastically change its double bond character. In the same solvent system cyclopentadithiophens (CH_2 instead of C=O) decompose, but in CF_3CO_2H at -15 °C three compounds gave ring-protonated species which were stable enough to be studied spectroscopically.



We now report that cyclopentadithiophenones are not protonated in CF_3CO_2H, but form strong hydrogen bonds instead. The hydrogen bonded species were studied by electronic absorption and ^{1}H and ^{13}C n.m.r. spectroscopy. In order to explain the observed properties on a quantitative basis, PPP calculations are presented in which hydrogen bond formation is interpreted in terms of charge displacements in the σ-skeleton of the carbonyl group.



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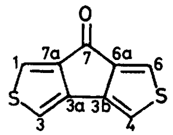

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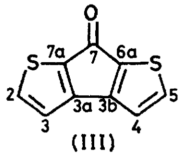

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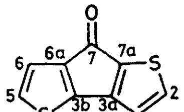

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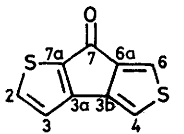

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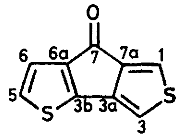

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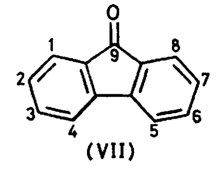

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RESULTS AND DISCUSSION

Electronic Absorption Spectra.—In cyclohexane, the cyclopentadithiophenones display weak lowest singlet–singlet transitions, λ 342—472 nm (ε 186—1 250), similar to fluorenone, λ 370 nm (ε 350), for which this band was assigned to a π–π* transition.[2-4] In 95% ethanol, these absorptions shift 10—21 nm towards longer wavelengths as expected for a π–π* transition of ketones for a change to a more polar solvent. The magnitude of these shifts is comparable to the shift of the corresponding band of fluorenone.[2] Therefore, the longest wavelength absorptions of the cyclopentadithiophenones can also be assigned to a π–π* transition. The fact that PPP calculations (see below) correctly predict the experimental transitions underlines this assignment. When the solvent is changed from cyclohexane to trifluoroacetic acid (at -15 °C) the longest wavelength absorption bands of cyclopentadithiophenones show remarkable shifts (44—73 nm; Table 1). New absorption bands do not appear. The corresponding transition of fluorenone shows a similar, although less striking shift (25 nm).

Dissolved in various mixtures of CF_3CO_2H and H_2O, all bands showed a continuous shift towards longer wavelength going from H_2O to CF_3CO_2H. These shifts are not due to a change in polarizability of the solvent since the spectra in a 3% solution of CF_3CO_2H in benzene and in pure CF_3CO_2H are almost identical.

The positions of the absorption bands in acetic acid are comparable with the positions in 95% ethanol. Therefore, the large shifts observed on changing the solvent from CH_3CO_2H to CF_3CO_2H must be attributed to the stronger proton donating power of CF_3CO_2H. The absence of a new strong absorption band, as observed when fluorenone is protonated at the oxygen atom,[5,6] excludes protonation, whereas the absence of band-broadening excludes a fast equilibration between ketone and conjugated acid. Therefore, the observed large red shifts of the absorption bands of the ketones are most probably due to strong hydrogen bond formation between the carbonyl oxygen atom and CF_3CO_2H.

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TABLE 1

Experimental and calculated transitions of cyclopenta*dithio*phenones and fluorenone in cyclohexane and CF_3-CO_2H (−15 °C). The transitions in CF_3COH_2 are given from 270 nm (the cut-off wavelength of CF_3-CO_2H) upwards

	Cyclohexane				CF_3CO_2H			
	Experimental		Calculated		Experimental		Calculated	
Ketone	λ/nm	$10^{-3}\epsilon$	λ/nm	*f*	λ/nm	$10^{-3}\epsilon$	λ/nm	*f*
(I)	472	1.3	457	0.171	545	0.6	532	0.100
	297sh	5.5	293	0.094	335sh	3.5	315	0.176
	285sh	7.0	292	0.481	304	5.0	302	0.218
	266	32.1	269	0.172			280	0.415
(II)	342	1.1	312	0.003	400sh	0.6	353	0.006
	305	5.2						
	299	4.0						
	291	6.8	280	0.021	335	6.1	299	0.098
	286sh	5.7						
	281	6.5	268	0.041	288	4.7	275	0.044
	275sh	8.7						
(III)	418	0.2	463	0.005	485	0.4	541	0.000
	337	10.2	321	0.177	362	9.1	341	0.423
	330	5.9						
	321	10.2	311	0.386	347sh	8.5	332	0.200
	311	6.8						
(IV)	459	0.4	450	0.064	510	0.2	526	0.032
	334sh	2.4						
	321	2.7	313	0.278	346	7.2	337	0.295
	298	4.8	293	0.296	313	6.7	308	0.175
							271	0.238
(V)	377	0.8	364	0.099	421	0.8	410	0.066
	326	3.5						
	319	3.3						
	312	4.5	298	0.118	338sh	5.9	322	0.308
	300	3.7			315sh	4.6		
	290	7.6	290	0.227	302	5.4	299	0.143
	279	6.5						
(VI)	380	0.6	360	0.159	437	0.4	408	0.083
					339sh	1.7		
	306sh	2.2	296	0.038	327	2.1	308	0.021
	295sh	3.2	273	0.247	290sh	7.3	287	0.323
	268	44.0	268	0.730	270	45.1	268	0.879
(VII)	370	0.4	355	0.101	395	0.2	398	0.056
	318	0.5			333	24.8		
	312	0.7	310	0.096	320sh	2.3	322	0.071
	305	2.1						
	292	4.2	305	0.001	302	2.7	313	0.081
	281	3.1			290sh	1.8		

N.m.r. Spectra.—^1H and ^{13}C n.m.r. spectra were recorded in $CDCl_3$ and CF_3CO_2H or CF_3CO_2D (at −15 °C). The analyses of the ^1H and ^{13}C n.m.r. spectra in $CDCl_3$ were presented earlier.[7,8] The assignments of the resonances in $CF_3CO_2H(D)$ were based on the chemical shifts in $CDCl_3$. The large difference in intensity of the tertiary and quaternary carbon atoms was also used for their differentiation. In some cases, using CF_3CO_2D as a solvent, hydrogen–deuterium exchange was observed which was used for the assignment [9,10] (see Experimental section). Chemical shifts in CF_3CO_2H (^{13}C n.m.r. spectra) and the differences of the chemical shifts in CF_3CO_2H and $CDCl_3$ are compiled in Table 2.

The ^1H chemical shifts in CF_3CO_2H were found −0.03 upfield to +0.23 p.p.m. downfield compared with those in $CDCl_3$. The ^{13}C chemical shifts moved −2.4 to +7.0 p.p.m. on going from $CDCl_3$ to CF_3CO_2H. For the structural element C–H the changes in ^1H and ^{13}C chemical shifts were inter-related. Least-squares analysis gave the correlation $d\Delta\delta^{13}C/d\Delta\delta^{1}H = 24$ (*r* 0.97, *n* 18), which means that ^{13}C n.m.r. is 24 times more sensitive to charge delocalisation than ^1H n.m.r. This factor is almost the same as the values of 22 and 20, reported for the correlation of chemical shifts of the *para*-substituent in monosubstituted benzene derivatives.[11,12] For the structural unit depicted below the downfield shifts of the ^{13}C resonances are much larger for the β- and δ-positions (2.7—7.0 p.p.m.) than for the γ-position (0.9—1.2 p.p.m.). This order is reversed for the β′- and γ′-positions; now the downfield shift is largest for the γ′-carbon atom.

The α-carbon atoms are shifted upfield (−0.4 to −2.4 p.p.m.) and large downfield shifts are observed for the carbonyl carbon resonances (+6.0 to +6.8 p.p.m.). These results can readily be explained by hydrogen bonding to or protonation of the carbonyl group in CF_3CO_2H. The increase of positive charge on the carbonyl carbon results in a downfield shift in the ^{13}C n.m.r. spectrum. This positive charge will be delocalised over the π electronic system of the ketones, causing a downfield shift of β- and δ-carbon atoms. In compounds (I), (III), and (IV) the β- and δ-tertiary carbon atoms show larger downfield shifts than the quaternary β- and δ-atoms C(3a) and C(3b). Probably the central ring, which may be described in these compounds as a formal cyclopentadienone ring, is not able to stabilize a positive charge in order to avoid becoming ' anti-aromatic '. The ^{13}C resonances of fluorenone have changed much more in H_2SO_4 than in CF_3CO_2H, compared with $CDCl_3$. These much larger shifts in H_2SO_4 rule out the possibility of complete protonation in CF_3CO_2H. In the case of a fast equilibrium between protonated and ' free ' ketone in CF_3CO_2H all resonances should have shifts that are intermediate between those in H_2SO_4 and $CDCl_3$. Since this was not observed, only hydrogen bonding satisfactorily explains the experimental results.

The ^1H n.m.r. spectra of the ketones in CF_3CO_2H support this conclusion. Compared to the spectra in $CDCl_3$ the chemical shifts of H(1) and H(6) in (II) shift 0.23 p.p.m. downfield. In FSO_3H–SbF_5–SO_2 at −60 °C, in which the carbonyl oxygen is protonated, the same protons of (II) shift as much as 0.69 p.p.m. downfield.[1]

PPP Calculations.—In order to study whether the influence of hydrogen bond formation on the electronic absorption and n.m.r. spectra can be explained in terms of MO theory, PPP calculations [13,14] were carried out. Details of the calculations have been reported elsewhere.[1] The parameters used are given in Table 3.

The O–H bond in the hydrogen bonded carbonyl group (below) may be considered to be intermediate

$$=O^{+\delta Q} \cdots H^{+1-\delta Q}$$

between a complete covalent bond, as in the case of protonation (δQ 1), and non-bonded (δQ 0), as in the case

TABLE 2

^{13}C N.m.r. chemical shifts (p.p.m.) in CF$_3$CO$_2$H; ^{1}H and ^{13}C n.m.r. solvent shifts (p.p.m.) in CFCO$_2$H (compared with CDCl$_3$) and the calculated (δQ 0.25) changes in charge due to hydrogen bonding

Compound	Atom	$\Delta\delta(^1H)$	$\delta(^{13}C)$	$\Delta\delta(^{13}C)$	ΔQ	Atom	$\delta(^{13}C)$	$\Delta\delta(^{13}C)$	ΔQ
(I)	1, 6	−0.03	121.9	0.5	0.005	3a, 3b	151.8	3.0	0.013
	2, 5	0.03	128.3	1.5	0.012	6a, 7a	141.7	−0.5	−0.022
						7	188.6	6.4	0.062
(II)	1, 6	0.23	133.7	7.0	0.024	3a, 3b	141.2	0.5	−0.001
	3, 4	0.04	117.9	2.8	0.014	6a, 7a	146.1	−1.9	−0.210
							184.6	6.0	0.054
(III)	2, 5	0.14	140.9	4.7	0.023	3a, 3b	154.6	3.0	0.017
	3, 4	−0.01	120.7	1.2	0.007	6a, 7a	135.4	−1.2	−0.026
						7	171.2	6.8	0.054
(IV)	2	0.14	141.6	5.0	0.023	3a	152.6	3.0	0.018
	3	−0.02	120.2	0.9	0.006	3b	153.0	2.7	0.011
	5	0.03	128.3	1.8	0.013	6a	142.7	−0.4	−0.019
	6	−0.02	122.6	0.6	0.005	7a	134.2	−1.4	−0.028
						7	187.6	6.5	0.059
(V)	2	0.23	144.2	6.0	0.025	3a	157.9	4.8	−0.022
	3	0.04	121.2	1.2	0.004	3b	139.5	−0.1	0.006
	4	0.08	117.4	3.3	0.022	6a	143.2	−1.1	−0.019
	6	0.19	131.6	5.4	0.026	7a	141.6	−2.2	−0.027
						7	184.8	6.6	0.051
(VI)	1	0.17	131.2	5.7	0.026	3a	138.2	−0.2	−0.005
	3	0.06	118.1	3.9	0.022	3b	158.7	5.5	0.017
	5	0.05	129.9	1.8	0.011	6a	147.2	−1.7	−0.022
	6	0.00(4)	121.8	0.6	0.003	7a	141.7	−2.4	−0.020
						7	186.0	6.4	0.056
(VII)	1, 8		125.2	1.1	0.012	10, 13	133.2	−0.6	−0.025
	2, 7		129.3	0.6	0.008	11, 12	145.1	1.1	0.006
	3, 6		136.6	2.3	0.019	9	199.6	6.3	0.065
	4, 5		120.5	0.6	0.009				
(VII)	1, 8		132.3	8.4		10, 13	130.7	−3.1	
(H$_2$SO$_4$)	2, 7		133.1	4.4		11, 12	148.1	4.1	
	3, 6		145.6	11.3		9	205.4	12.2	
	4. 5		124.6	4.7					

of the free ketone. The positive charge on hydrogen leads to displacement of the oxygen σ-electrons. This has been accounted for in the π-electron calculations by modifying the core parameters as a function of the core charge following the expressions given by Nishimoto *et al.*[15] Parameters for the core charges +1 and +2 given in Table 3, represent the limits for the free and protonated oxygen atom, respectively.

The value of δQ was varied and the calculated shifts of the longest wavelength transitions in the electronic absorption spectra due to hydrogen bonding were compared with the experimental shifts. The value δQ +0.25 gave the best results (Table 4) and was used to describe the hydrogen bonding of cyclopentadithiophenones in CF$_3$CO$_2$H.

The calculated transitions of the ketones in cyclohexane and CF$_3$CO$_2$H are shown in Table 1. In general, good agreement is observed between the experimental and calculated bands in cyclohexane. The transitions of ketone (II), however, are calculated at too low energy, as is the first band of ketone (III). The remainder of the calculated spectrum agrees well with the experimental bands. In CF$_3$CO$_2$H the first transitions of the same ketones (III) and (II) are calculated at too low and too high energy, respectively, but here too the remainder of the spectra of (II) and (III) as well as the transitions calculated for ketones (I), (IV)—(VI), and fluorenone are in very good agreement with the observed values. The conclusion that cyclopentadithiophenones are not protonated in CF$_3$CO$_2$H is also supported by the results of the calculations of the transitions of the protonated ketones (δQ +1). For each ketone the calculations predict a strong extra band at 405—457 nm and a very large red shift of the longest wavelength absorption, in contrast with the experimental results.

TABLE 3

Semiemperical parameters for the PPP calculations *

Atom	I_X(eV)	γ_{XX}(eV)	β_{CX}(eV)	Core charge
C	11.22	10.53	f(p) †	+1
S	20.00	10.84	−1.625	+2
O	13.60	11.30	f'(p) ‡	+1
	17.36	13.48	f'(p)	+1.25
	30.88	20.03	f'(p)	+2

* C–O bond distance 1.26 Å. † $\beta_{CC} = -0.51p - 1.84$ eV. ‡ $\beta_{CO} = -0.56p - 2.20$ eV.

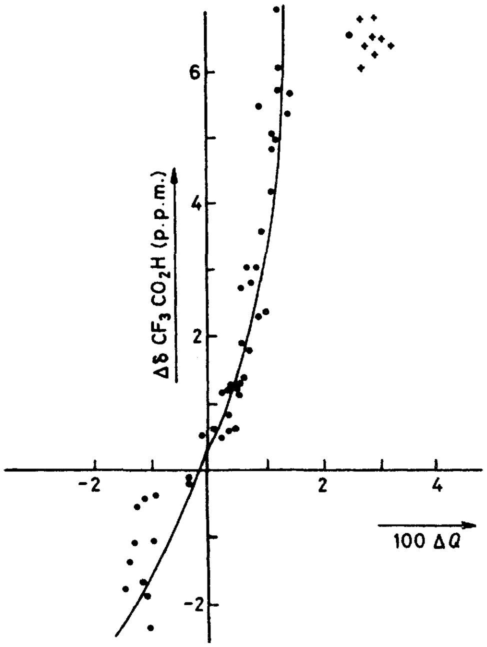
TABLE 4

The experimental and calculated (δQ +0.25) shifts of the longest wavelength transitions in the electronic absorption spectra of the cyclopentadithiophenones and fluorenone in CF$_3$CO$_2$H

Ketone	$\Delta_{experimental}$/ nm (kK *)	$\Delta_{calculated}$/ nm (kK)
(I)	73 (2.9)	75 (3.1)
(II)	58 (4.2)	41 (3.8)
(III)	67 (3.3)	78 (3.1)
(IV)	51 (2.2)	76 (3.2)
(V)	44 (2.7)	46 (3.1)
(VI)	57 (3.1)	48 (3.3)
(VII)	25 (1.7)	43 (3.1)

* 1 kK = 1 000 cm^{-1}.

The differences in charges as calculated for each carbon atom in the free and hydrogen bonded ketone, are, together with the observed ^{13}C and ^{1}H n.m.r. chemical shift differences, summarized in Table 2. The correlation between the calculated changes in electron density and the ^{13}C chemical shift is given in the Figure. The results show that a simple linear correlation does not exist. The data for the carbonyl atoms are situated in a group apart from the other carbon atoms. When the carbonyl carbon atoms are excluded from the correlation, a curved line is obtained of which the slope varies from 120 to 240 p.p.m./el. Least squares analyses gave the following results: all carbon atoms except those of the carbonyl group, $d\Delta\delta^{13}C/d\Delta Q$ 128 ± 10 p.p.m./el (r 0.90, n 42), tertiary carbon atoms, $d\Delta\delta^{13}C/d\Delta Q$ 236 ± 20 p.p.m./el (r 0.95, n 22), and $d\Delta\delta^{1}H/d\Delta Q$ 9 ± 1 p.p.m./el (r 0.89, n 22). The values for the relation of $\delta^{13}C$ and $\delta^{1}H$ and charge correspond to the values of 160—200 p.p.m./el ($\delta^{13}C$)[16] and 8—10.6 p.p.m./el ($\delta^{1}H$)[12,17] reported earlier.



Correlation of ^{13}C solvent shifts of cyclopentadithiophenones in CF_3CO_2H and the calculated changes of charge (+, carbonyl carbon atoms)

EXPERIMENTAL

Cyclopentadithiophenones and fluorenone were obtained from stock or prepared by standard methods[18,19] and purified by sublimation *in vacuo*. Commercially available 95% ethanol, cyclohexane, $CDCl_3$, CF_3CO_2H, and CF_3CO_2D (Merck; Uvasol) were used.

MO Calculations were performed on the Telefunken TR-4 and CDC Cyber 74-16 computers of the Computing Center of the University, Groningen. The PPP program was based on the Householder method for the determination of eigenvalues and eigenvectors.

U.v. spectra were recorded on a Cary 15 spectrophotometer equipped with a Cryoson TRL1B variable temperature control unit.

N.m.r. spectra were recorded on a Varian XL-100/15 spectrometer with variable temperature probe. $CHCl_3$ was used as an internal standard in the ^{1}H n.m.r. measurements. In the ^{13}C n.m.r. experiments chemical shifts were measured relative to the CF_3 resonance and converted to Me_4Si as reference using known relationships between the chemical shifts of CF_3, $CHCl_3$, and Me_4Si.

Assignment of ^{13}C *N.m.r. Resonances.—Compound* (I). The resonance at δ 128.3 p.p.m. present in the spectrum of a freshly prepared solution in CF_3CO_2D slowly changes into a triplet. This resonance has to be assigned to C(2) and C(5), since H–D experiments[9,10] have shown that exchange occurred at these sites. The quaternary carbon resonance at δ 151.8 p.p.m., with half the intensity of the resonances at δ 141.7 p.p.m., is assigned to C(3a) and C(3b).

Compound (III). The quarternary resonance at δ 135.4 p.p.m. is, because of its low intensity, assigned to C(6a) and C(7a).

Compound (IV). A tertiary resonance is hidden by a solvent peak at δ 120.2 p.p.m., as shown by the noise decoupled spectrum of (IV) in $CDCl_3$–CF_3CO_2H (6 : 1) which reveals a resonance close to that of CF_3CO_2H. The quaternary resonances at δ 153.0 and 134.2 p.p.m. are, because of their low intensity, assigned to C(3b) and C(7a).

Compound (V). One tertiary resonance is hidden by a solvent peak. The coupled spectrum showed a doublet (J_{CH} 190 Hz) with both satellites at equal distance of the solvent peak. The small resonance at δ 141.6 p.p.m. is assigned to C(7a).

Compound (VI). The tertiary resonances are assigned with the help of the coupling constants obtained from the coupled spectrum. The resonance at δ 121.8 p.p.m., displaying a one-bond coupling constant of 177 Hz, must be that of a β-thiophen carbon atom and is assigned to C(6). Of the three remaining tertiary resonances, with α-thiophen C–H coupling constants of 190 Hz, two resonances have a long-range coupling constant of 5 Hz and the third 7 Hz. This last resonance (δ 129.9 p.p.m.) is, by analogy with the assignment for $CDCl_3$, assigned to C(5). The small quaternary resonance at δ 158.7 p.p.m. is assigned to C(3b).

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