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CHARGE-TRANSFER COMPLEXES OF SOME CHLOROCARBON KETONES

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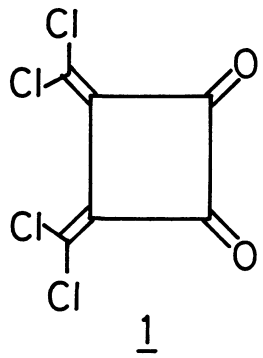
The reactions of five chlorocarbon ketones with N,N,N',N'-tetramethyl-p-phenylenediamine or N,N-dimethylaniline were examined. Two of them afforded stable outer complexes with the former amine, while the rests gave very unstable complexes only evidenced by their CT-bands. Substituted products were only obtained in the reactions of all the ketones with the latter.

The recent interest in stable charge-transfer (CT or D-A (donor-acceptor)) complexes has been focussed on the properties as semiconductor.[1] Among many chlorocarbon ketones, only o- and p-chloranils (CA) have been well known as good electron acceptors with low LUMO levels, giving stable crystalline CT complexes with aromatic amines[2] and hexamethylbenzene.[3]

We wish to report the syntheses of the complexes of amines with two CA isomers (perchloro-3,4-dimethylene-1,2-cyclobutanedione (1)[4] and -2-methylenecyclopent-4-ene-1,3-dione (2)[5]), whose LUMO levels are expected to be sufficiently low. Examinations were also made for the possibility of complex formation with three related ketones, perchloro-2,3-dimethylenecylobutanone (3),[6] -2-methylenecyclopent-4-enone (4),[5] and -cyclopentene-1,4-dione (5).[7] HMO calculation (Table 1) suggests that all the ketones except 4 have the LUMO level, which is a little higher than that of CA, but still significantly low to cause the reactions with aromatic amines such as N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) and N,N-dimethylaniline (DMA).



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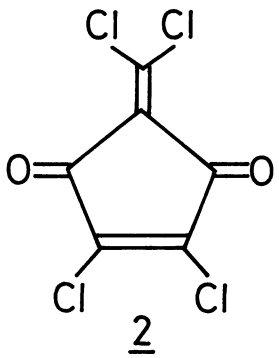

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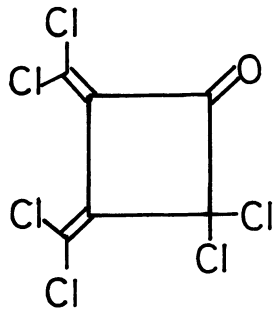
Table 1. Coefficient of the Eigenvalue, $E_{LUMO} = \alpha + X_{LUMO}\beta$[8]

Compound	X_{LUMO}
1	-0.085
2	-0.060
3	-0.082
4	-0.313
5	-0.060
CA	+0.177
Tetracyanoethylene	-0.029
Benzene	-1.000



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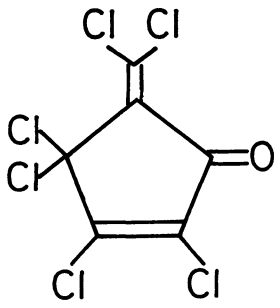

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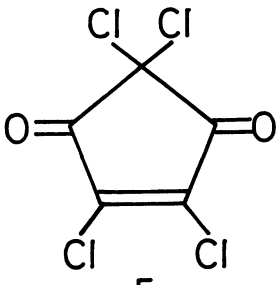

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When 1 was reacted with TMPD in hexane at room temperature under nitrogen atmosphere, two kinds of products were obtained; black crystalline powder (1:2 D-A complex) (6) and blue-black crystals (1:1 D-A complex) (7). The isomeric ketone 2 also reacted smoothly with the amine in benzene under the same conditions to give only the blue-black crystals of a 1:1 D-A complex (8).

The complexes 6 - 8 are stable in the air for several days and stand in a refrigerator for a month or more without remarkable decomposition. In all cases, a rapid and complete dissociation to the components takes place upon high dilution with nonpolar solvent, resulting in the disappearance of the CT absorption band which is sometimes observable with the saturated solution (Fig. 1). The markedly different CT bands of the complexes in KBr pellet are also shown in Fig. 2. In the polar solvent like acetonitrile, the complete electron transfer occurs, which is simply evidenced by the disappearance of the CT band and the appearance of the typical intense absorption of the Würster-blue cation ($TMPD^+$). Their IR spectra are very close to the superposition of those of the components only with some slight shifts of $\nu_{C=O}$ and $\nu_{C=C}$ bands, revealing that they are of the type of outer complex.[9] The spectral data, mp's and yiels are listed in Table 2.

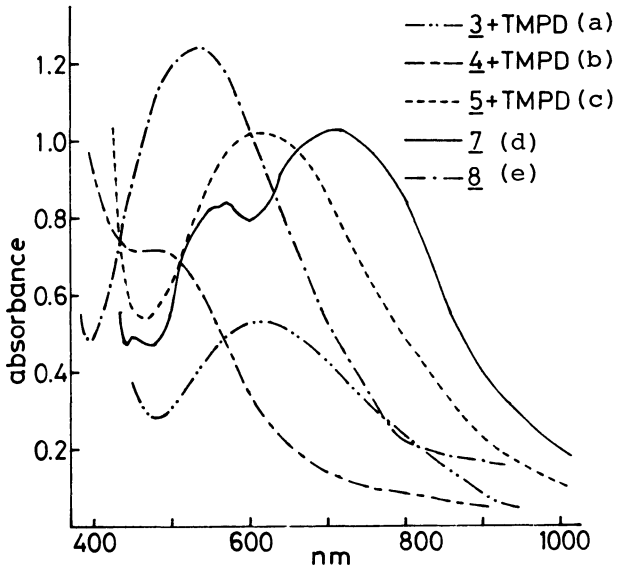

Fig. 1. The absorption spectra of the complexes in hexane. For the concentrations, see note 10.

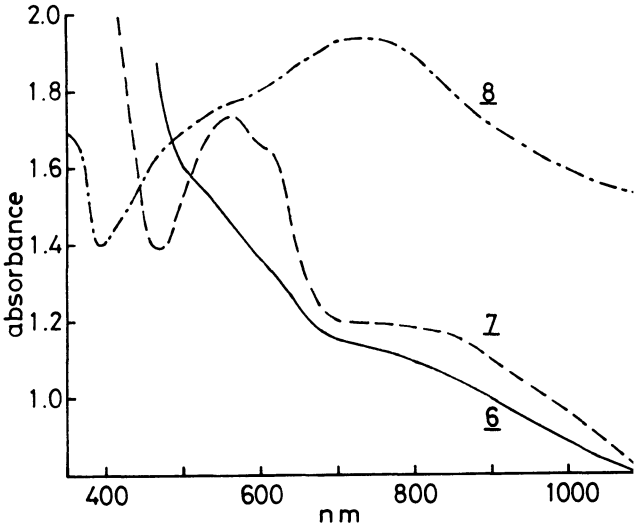

Fig. 2. The absorption spectra of 6 - 8 in KBr pellet.

Table 2. Physical Data and Yields of 6, 7, and 8[a]

	IR(Nujol)(cm^{-1})		CT Band (λ_{max}, nm)		Mp(°C)	Yield(%)
	$\nu_{C=O}$	$\nu_{C=C}$	KBr-Pellet	Soln.(Hexane)		
6	1799m, 1745vs	1604s, 1518s[b]	520sh[c], 610sh[c], 800sh	——[d]	87(dec)	18.3
7	1794m, 1775m, 1742vs	1616s, 1515s[b]	565[c], 610sh[c], 800sh	447[e], 560[e], 700(ε 93)	74(dec)	42.7
8	1750m, 1716vs	1632m, 1595vs, 1523s[b]	360sh[c], 480sh[c], 740	530(ε 70)	104(dec)	81.3
1	1813m, 1767vs	1604s, 1521s	——	——	167	—
2[f]	1724vs	1631vs	——	——	231	—

a. Elemental analyses are satisfactory. b. Bands due to the amine component ($\nu_{C=C}$ 1519vs). c. Locally excited bands; the values are almost the same as those of the ketonic components. d. Conversion into 7. e. Due to the dissociation to the components. f. E. T. McBee, H. E. Ungnade, H. Rakoff, and K. Dingberg, J. Am. Chem. Soc., 77, 4379 (1955).

Other related ketones 3, 4, and 5 also formed CT complexes with TMPD in hexane giving their CT bands at 620, 485, and 610 nm, respectively (Fig. 1). The complexes are, however, so unstable in the saturated solution that attempts to isolate them even under careful work-up have not been successful. The instabilities seem to be attributed to the out-of-plane allylic chlorine substituents which would make the orbital overlap between D and A insufficient, or would react further with the amine in a different way. All the ketones 1 and 5 reacted with TMPD in acetonitrile to give the Würster-blue cation easily characterized by the absorption spectra.[11]

The reactions of 1, 2, 3, and 5 with DMA, a less reactive electron donor than TMPD, both in polar and nonpolar solvents, gave only the substitution products, 9, 10, 11, and 12, respectively. Since, in all cases, no CT bands were detected in the spectra taken at room temperature, the substitution reactions would proceed very rapidly via the corresponding complexes. Interestingly, an N-substituted product (13) was also obtained in the case of 5. Compounds 9 - 12 are all deeply colored, probably because of the zwitter-ionic resonance structures. Their spectral data all agree with the structures given below. The existence of a 1,2-dionic group in 9 was evidenced by the formation of a quinoxaline derivative (14). In contrast to the reaction of CA with DMA, no crystal violet salt[12] was detected in the present work. The ketone 4 did not react at all with DMA, reflecting its low value of X_{LUMO}.

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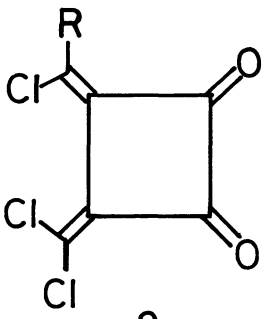

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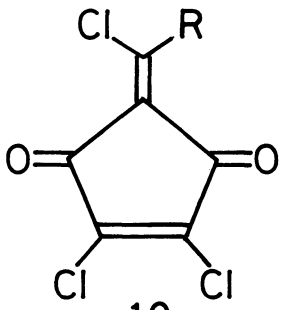

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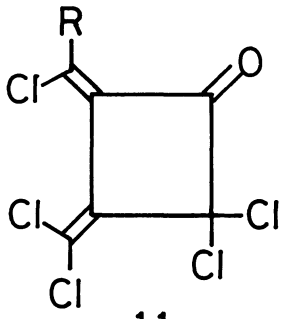

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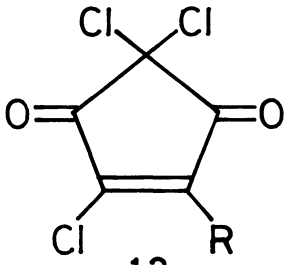

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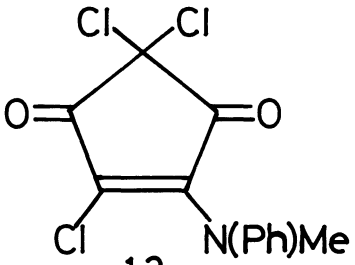

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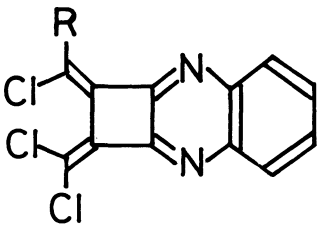

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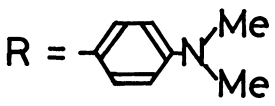

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8) Parameters for the heteroatoms in calculation were taken from A. Streitwieser, Jr., " Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, 1961, P. 121, 126.
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10) The concentrations were: a) 3(4.4) + TMPD(1.1); b) 4(2.7) + TMPD(2.2); c) 5(4.8) + TMPD(3.1); d) 1.1; e) 1.8 (x 10^{-2}mol/l). Cell length: 1cm.
11) The absorption bands corresponding to the counter anions were not confirmable because of the overlapping with that of $TMPD^{+}$, intense near 330 nm. In the reactions with 1 and 3, they were exceptionally observed at 443 and 394 nm, respectively.
12) J. W. Eastman, G. Engelsma, and M. Calvin, J. Am. Chem. Soc., 84, 1339 (1962).

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