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ELECTRONIC EFFECT OF SOME EPOXIDES AND CYCLOPROPANES. HYPERCONJUGATIVE ELECTRON WITHDRAWAL

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Abstract—Charge transfer absorption frequency and carbon nuclear magnetic resonance studies of epoxides and cyclopropane derivatives have given information about the electronic effects of these small rings. The epoxide group is strongly electron-withdrawing from an aromatic ring by hyperconjugative and inductive effects. Dichlorocyclopropane withdraws electrons inductively. The tosylimino group is also electron-withdrawing. These conclusions were drawn from the comparison with open chain analogues.

Through it is well known that the cyclopropane ring is remarkably effective at stabilizing a cationic center,[1] the electronic interaction of oxirane, a strained hyterocyclic small ring, with adjacent unsaturated groups has not been established. Rogers[2] and Cromwell[3] demonstrated that oxirane can transmit as well as extend electronic effects in various substituted chalcone oxides, and introduced hyperconjugative concepts. More recently, Strait showed that the oxirane ring acts as an electron acceptor from an aromatic ring.[4] However these studies did not take account of inductive effects and the conclusion seems rather uncertain. The purpose of the present research is to provide physicochemical studies on the electronic effect of the oxirane ring and related groups.

EXPERIMENTAL

Compounds which we submitted to this study were 9,10-dihydrophenanthrene **1**,[5] m.p. 40–42°, 9,10-methano-9,10-dihydrophenanthrene **2**,[6] m.p. 69–70°, 9,10 - (dichloromethano) - 9,10 - dihydrophenanthrene **3**,[7] m.p. 148–9°, 9,10 - epoxy - 9,10 - dihydrophenanthrene **4**[8] m.p. 134–5° (when heated rapidly), 9,10 - tosylimino - 9,10 - dihydrophenanthrene **5**,[9] m.p. 168–171°, *cis* - 9,10 - dihydroxy - 9,10 - dihydrophenanthrene **6**,[10] m.p. 170–1° (decomp.), *trans* - 9,10 - dihydroxy - 9,10 - dihydrophenanthrene **7**,[11] m.p. 175–8° (decomp.), cyclopropylbenzene **8**,[12] b.p. 169–171°, (2,2 - dichlorocyclopropyl)benzene **9**,[13] b.p. 112–3°/15 mm Hg, styrene oxide (Tokyo Kasei) **10**, b.p. 193°, isopropylbenzene(Wako) **11**, b.p. 152°, *β,β*-dichloroethylbenzene **12**[14] b.p. 110–1°/25 mm Hg, and benzyl methyl ether **13**,[15] b.p. 170°. Tetracyanoethylene (Tokyo Kasei) was purified by sublimation, m.p. 199°. Merck chloroform-d was used. Dichloromethane was Dotite spectral grade.

The carbon-13 Fourier transform NMR spectra were obtained at 100 MHz with a Jeol PS-100. All hydrogens were noise-decoupled. Samples were examined at concentration of 3–7% in $CDCl_3$ solution at room temperature.

Charge transfer spectra were obtained with a Hitachi EPS-2U instrument at 25°. To a methylene chloride solution of a compound (about 5 mg in 3 ml) was added a powdered tetracyanoethylene (1–5 mg) using a 1 cm path cell and a reference cell containing methylene chloride, and spectra were recorded immediately after mixing.

RESULTS AND DISCUSSION

The carbon-13 nuclear magnetic resonance (CMR) chemical shifts of dihydrophenanthrene **1** and 9,10 - cyclo - substituted dihydrophenanthrenes **2**, **3** and **4** are shown in Fig. 1. According to the relationship between chemical shift and electron density,[16] the lower chemical shifts of aromatic carbons, probably of the positions 1 and/or 3, in compounds **3** and **4** show the electron deficient character of the positions (shown by arrows in Fig. 1), whereas the aromatic carbons of **2** are electron-rich. Similar results were obtained from CMR of substituted benzenes.[17] Thus, a qualitative conclusion can be obtained that an oxirane ring and a dichlorocyclopropane ring are electron withdrawing from an aromatic ring.

A more quantitative observation from the absorption bands of charge transfer (CT) complexes with tetracyanoethylene(TCNE) clearly reveals the electronic effect of these groups. The CT absorption bands of dihydrophenanthrene derivatives **1–7** and monosubstituted benzenes **8–13** with TCNE in methylene chloride were listed in Table 1. The CT absorption frequencies have been well correlated with σ^* by extensive works of Traylor.[18] The relationship is quite useful in evaluating

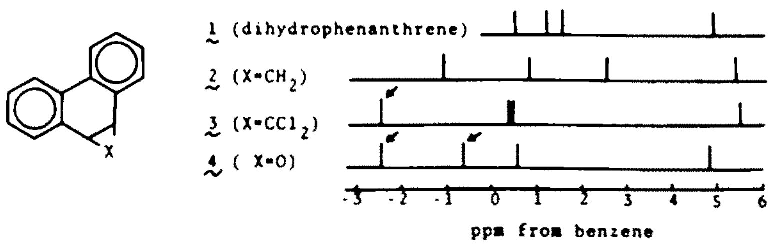
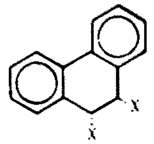
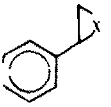
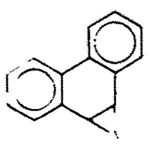
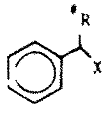


Fig. 1. Chemical shifts of aromatic carbons of dihydro phenanthrenes.

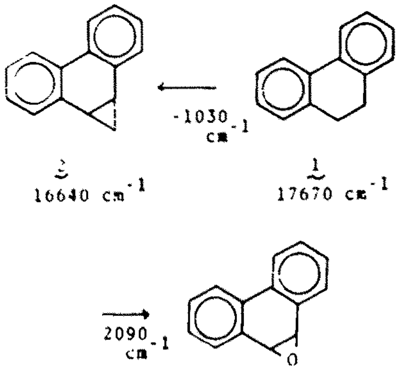
Table 1. Charge transfer absorption frequencies of TCNE complexes in CH_2Cl_2

Compound		X*	The first CT mμ (cm^{-1})	The second CT mμ (cm^{-1})	Compound		X*	The first CT mμ (cm^{-1})
	1	H	566(17670)	425(23530)		8	CH_2	480(20830)
	6	OH(trans)	535(18690)	406(24630)		9	CCl_2	395(25230)
	7	OH(cis)	520(19230)	415(24100)		10	O	375(26670)
	2	CH_2	601(16640)	454(22020)		11	CH_3	418(23920)
	3	CCl_2	546(18320)	422(23700)		12	$CHCl_2$	390(25640)
	4	O	506(19760)	390(25640)		13	OCH_3	394(25380)
	5	NTs	503(19880)	410(24390)				

*R=CH_3 11, H 12 and 13.

substituent effects. As established in cyclopropylbenzene,[1] the cyclopropane group of 2 works as an electron donor to the biphenyl moiety, revealed by the comparison of the CT frequency of 2 with that of a reference compound, 1. Dihydrophenanthrene 1 may not be the best compound as the reference, two benzene rings of the biphenyl being twisted because of the flexible ethylene bridge. However, the energy difference between the calculated HOMO levels for two interplanar angles of bephenyl moiety, 0° and 17.52°, is small.[19]

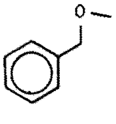
On the other hand, the oxirane ring of 4 is quite strongly electron-withdrawing. The effect of the oxirane ring is much larger, to the opposite direction, than that of the cyclopropane ring: $\nu_4 - \nu_1 = 2090\ \text{cm}^{-1}$ and $\nu_2 - \nu_1 = -1030\ \text{cm}^{-1}$. Introduction of two chlorine atoms onto the cyclopropane ring of 2 does suppress the large electron-donating effect of the cyclopropane ring. The tosylimino group of 5 has a similar effect to that of the oxirane ring. The same result was obtained from the comparison of cyclopropylbenzene 8, dichlorocyclopropylbenzene 9, and styrene oxide 10.



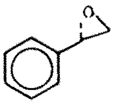
4

19760 cm^{-1}

The CT bands of dihydroxydihydrophenanthrenes 6 and 7 indicate that the hydroxyl group is electron-withdrawing by inductive effect when compared with 1. However, the formation of a three membered oxirane ring increases the electron-withdrawing effect (compare CT frequencies of 4 and 6, 7).[20]



13 25380 cm^{-1}

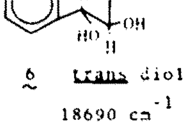


10 26675 cm^{-1}

The similar relation was observed in the CT frequencies of styrene oxide 10 and its open chain analogue, benzyl methyl ether 13. The oxirane ring of styrene oxide is more effectively electron-withdrawing than the methoxymethyl group which is more electron-withdrawing than the methoxymethyl group which is more electron-withdrawing than ethyl or isopropyl group. Therefore, the enhanced electron-withdrawing effect due to the oxirane ring on an aromatic ring should be the sum of the inductive effect of the oxygen atom and the other cause, which is induced by the formation of a strained ring, possibly hyperconjugative electron-withdrawal by the bent C–O bond.[21]

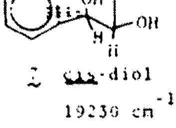
Dewar has recently proposed that the electronic effect of substituted methyl groups (CH_2–X, where X is more electronegative than carbon) can be attributed partly to hyperconjugative electron withdrawal by C–X bond when the conformation of C–X bond is favored.[22] The epoxide 4 satisfies the favorable conformation.[23] The higher frequency observed in the *cis*-diol 7 than the frequency of the *trans*-diol 6 is also attributed to the conformational effect. *cis*-Diol 7 has one C–O bond (though not strained) parallel to the benzenoid pi electron, therefore hyperconjugative interaction is possible, while both hydroxyl groups of 6 do not exist in such a parallel conformation.

The substitution on a cyclopropane ring by two chlorine atoms completely suppresses the large effect of



6 trans-diol

18690 cm^{-1}



7 cis-diol

19230 cm^{-1}

the bent C–C bonds of the cyclopropane ring. The dichloroethyl group suppresses the electron-donating effect of ethyl or isopropyl in a clearly inductive manner, judging from the comparison of the CT frequency of **12** with those of ethylbenzene (24,200 cm^{-1}) or of **11**. The CT frequency of dichlorocyclopropylbenzene **9** is nearly identical with that of **12**. No significant change was observed in forming a dichlorocyclopropane ring. Therefore, it may be concluded that the effect of the dichlorocyclopropane group is attributed to inductive withdrawal.[24] It is quite interesting that this effect is a contrast to the effect of oxirane ring discussed above though the inductive effect of $CHCl_2$, represented by σ^* or σ_I, is close to that of OCH_3.[25] The present view agrees with the observation by Kusuyama that the contribution of the resonance by 2,2-dichlorocyclopropyl is minor.[26] The slower solvolysis rate of 2,2-dichlorocyclopropylcarbinyl chloride than the rate of propyl chloride has been reported.[27] This is a reflection of the electron-withdrawing effect of the dichlorocyclopropane ring.

These results and discussion are summarized in Fig. 2. The cyclopropane hyperconjugatively donates electrons to the aromatic ring; the oxirane is inductively and hyperconjugatively electron withdrawing; and the dichlorocyclopropane withdraws electron inductively.

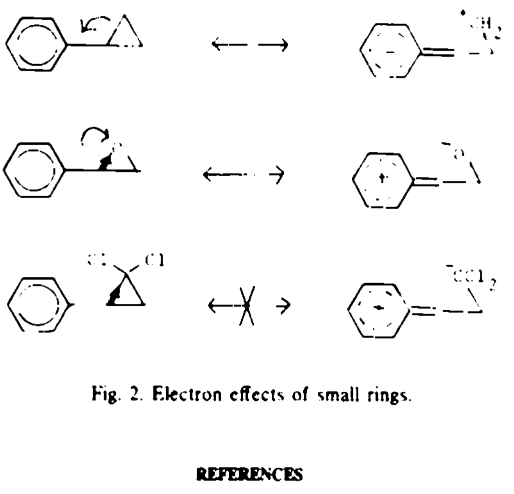


Fig. 2. Electron effects of small rings.

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[20] Contribution of the inductive effect by an oxygen atom in compound **4**, may be smaller than the observed effect of *trans* diol **7** which has two oxygen atoms per molecule.

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[24] A discussion is possible that the conjugative effect of the newly formed bent C–C bond (donating) and the newly formed bent $C-CCl_2$ bond (withdrawing) are almost cancelled out. In compound **3**, however, the $C_{(9)}-C_{(10)}$ bond cannot interact with the aromatic ring. The effect of dichlorocyclopropane ring of **3** is therefore reasonably accounted for simply by the inductive effect of the CCl_2 group.

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