Sulphuryl Chloride as an Electrophile. Part 5.[1] Chlorination of Some Anthracene Derivatives; Molecular Orbital Modelling of Substituent Effects

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The rates of electrophilic attack at C-10 of some 9-substituted anthracenes (9-H, Br, CHO, CN, NO_2, OMe, or Bz) by sulphuryl chloride have been measured (in PhCl 298 K). The substituent effects roughly parallel those expected from considering the simpler p-XC_6H_4 system (ρ −1.51; r 0.975); better agreement (ρ -1.23 ± 0.05; r 0.994) comes by using Dewar's FMMF treatment. MNDO calculations of the energy and optimised geometry of the intermediate σ-complex show a folded structure which allows a degree of sp^3 character of the C-10 atom while maintaining sufficient delocalisation of the extended π-system in the anthracenium ion. The Bell–Eyring–Polyani principle is followed with a linear correlation between the difference in the calculated energy between each reactant and its σ-complex and the experimentally observed change in free energy during attack by $Cl^{\delta+}$.

Studies of the transmission of substituent effects in aromatic systems are still mainly limited to consideration of the benzene system. Substituent effects in the naphthalene structure (exemplified by studies of n.m.r. chemical shifts,[2] e.s.r. properties of naphthyloxyl radicals,[3] and the dissociation constants of the appropriate acids, phenols, and amines[4]) have been relatively well defined, although not in every major field of chemical study.[5] In the biphenyl system, substituent effects have been shown generally to be transmitted from one phenyl ring to the other without selection between inductive and mesomeric contributions;[6] this deduction may also be made by considering substituent effects in some reactions of naphthalene derivatives.[7]

Studies of the corresponding effects in anthracene compounds have been relatively few, and even these have been criticised. Attack upon anthracene occurs almost entirely at the *meso*-(9- and 10-) positions;[8] although 10-substituted derivatives of 9-fluoro-[9a] and 9-carboxy-anthracene[9b,c] are the most easily obtained isomers, these are the sites most susceptible to steric effects. The separation of steric and electronic contributions, and so the experimental confirmation of theoretical parameters purporting to reflect substituent effects, is therefore difficult. The electrophilic[10] substitution of aromatic systems by sulphuryl chloride is quite sensitive to substituent effects in attack on derivatives of anisole (ρ −4.0)[10c] and also on alkylbenzenes (ρ −7) but seems to have only slight steric requirements: only a secondary steric effect could be demonstrated[1] in studies of highly congested methoxybenzene derivatives.

A study of the rates of electrophilic chlorination of derivatives of anthracene by sulphuryl chloride could therefore be complicated by secondary steric effects but would be unlikely to be affected by primary interactions around the reaction site. We now report the results of such a study, together with the applications of Dewar's FMMF calculation method[11] towards assessing the expected electronic effects of the substituents in the anthracene system, and the use of a much more fundamental MNDO calculation of the energies of each ground-state anthracene system and of the corresponding σ-complex formed by attack by Cl^+ upon C-10 of the anthracene derivative. Such studies have been made for benzene derivatives[12] and these show adherance to the Bell–Eyring–Polyani principle in which the energy of reaction and the energy of activation are linearly related; it was intended that similar calculations should be made for the 9-substituted anthracenes and their results compared with experiment.

Table 1. Organic products of attack by sulphuryl chloride upon substituted anthracenes

	Starting material		10-Chloro derivative	
Subst.	M.p. (°C) (lit. m.p.)	Yield (%)	M.p. (°C) (lit. m.p.)	Yield (%)
H	218 (218)[a]		105—106 (104—106)[b]	84
9-NO_2	145—146 (145—146)[c]	92	208—210 (220—221)[d]	84
9-Bz	148 (148)[e]	71	164—165 (164—165)[f]	84
9-Cl	105—106 (104—106)[b]	68		
9-Br	99—101 (98—99)[b]	72	205—207 (207)[g]	96
9-CN	177—178 (177.5—179.0)[h]	95	255—256 (255)[i]	94
9-CHO	104.5—105.0 (104.5—105.0)[j]	75	212—214 (215—216)[k]	89
9-Me	100 (100)[l]	64	178—179 (179—180)[m]	79
9-MeO	97—98 (97—98)[n]	64	148—150 (154)[o]	94

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Discussion

Table 1 shows that the major mode of reaction is described by equation (1). Although the molecular chlorination of

$$ArH + SO_2Cl_2 \longrightarrow ArCl + SO_2 + HCl \qquad (1)$$

anthracene gives both substitution and addition products,[8] we

Table 2. Rate constants and FMMF parameters for attack on substituted anthracenes (SO_2Cl_2 in PhCl at 298 K)

Subst.	10^4k_2/l mol^{-1} s^{-1}	σ_{sim} (C-9 attack)
H	11.5^a	0.000
9-OMe	83	-0.717
9-Me	42	-0.413
9-Br	7.8	0.157
9-Bz	6.0	
9-CHO	2.5	0.697^b
9-CN	0.71	0.963
9-NO_2	0.42	1.102
2-Me	27	-0.247
		-0.134^c
2-Cl	4.8	0.213
		0.331^c

[a] Per equivalent site. [b] Calculated for CO_2H. [c] Attack at C-10 (apparently less reactive site).

Table 3. Solvent effects upon rate constants (2-X-anthracenes; SO_2Cl_2 at 298 K)

X	$k_2(PhH)^a$	$k_2(PhCl)^a$	$k_2(o\text{-}C_6H_4Cl_2)^a$
H	6.7×10^{-4}	23×10^{-4}	240×10^{-4}
Me	3.8×10^{-4}	13.5×10^{-4}	135×10^{-4}

[a] In l mol^{-1} s^{-1}.

found no evidence of addition products in the corresponding reaction of sulphuryl chloride, although such adducts are formed with methylnaphthalenes and other arenes.[13] The only detectable organic products in the reaction mixture after the removal of solvent were the starting material, the 10-chloro derivative and, in the case of anthracene itself, 9,10-dichloroanthracene. More significantly, these reaction mixtures did not lose hydrogen chloride slowly after the removal of acid species by aqueous sodium hydrogen carbonate; adducts such as 9,10-dichloro-9,10-dihydroanthracene form hydrogen chloride at room temperature during their re-aromatisation,[8] and our evidence suggests that no such adducts were formed, although the method of isolation precludes the identification of small amounts of these materials.

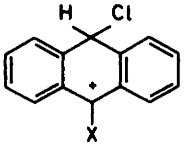
The second-order rate constants for the formation of sulphur dioxide during the attack upon the substituted anthracene did not diminish as the reaction proceeded; such behaviour was earlier used[10] to show that molecular sulphuryl chloride does not dissociate by the pre-equilibrium (2). The electrophilic

$$SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2 \qquad (2)$$

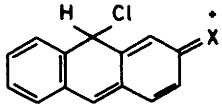
nature of the slow stage of the reaction is shown (Table 2) in the substituent effects; thus the methoxy group in the 9-position of anthracene speeds the reaction ($k_{OMe}/k_H = 7.2$). This acceleration is much less than that in the corresponding reactions of methoxybenzene derivatives ($k_{OMe}/k_H \simeq 2\,000$),[10c] and is not greatly different from that found in attack on 9-substituted anthracenes by trichloromethyl radicals ($k_{OMe}/k_H = 5.5$).[14] The sensitivity of the rate of the reaction to solvent effects is, however, very similar to that found in the corresponding attack upon 3,5-dimethylanisole and substantiates the belief that the essential nature of the slow step is heterolytic rather than homolytic (Table 3).

Among the compounds studied were two 2-substituted anthracenes. These were included to observe the effect of a more remote substituent upon the reaction rate; the results showed clearly that the 2-methyl group has little or no accelerating effect (*cf.* 9-methylanthracene), and that the 2-chloro substituent has a more pronounced depressant effect upon the reaction than does halogen in the 9-position. However, both 1-methyl and 2-methyl substituents are reported to direct incoming electrophiles strongly to one of the *meso*-positions; 2-methylanthracene gives mainly 2-methyl-9-bromoanthracene, and 1-methylanthracene undergoes attack at C-10.[15] Halogen substituents at these positions are also reported[16] to show similar directional effects; 1-chloroanthracene gives 9-bromo-1-chloroanthracene with phosphorus pentabromide in benzene. Such directional effects disgree with the kinetic observations of Table 2, in which, for example, anthracene and 2-methylanthracene are shown to have similar rates of attack.

While the explanation of this may be couched at various levels of sophistication, the resonance theory offers as simple an explanation as is needed. Attack at C-10 of the anthracene structure gives an anthracenium ion the most stable contributing structure of which is (1), in which two aromatic rings are retained. The loss of resonance energy has been calculated as *ca.* 11 kcal mol^{-1}, representing the difference in resonance energy between anthracene and two isolated benzene rings.[17] Any resonance interaction between this ion and a substituent at C-9 involves no further perturbation of the π-system. In contrast, structures (2) reflecting the interaction between a substituent at C-2 and either *meso*-position necessarily destroy aromaticity in two rings to give a higher-energy structure than that needed to reflect a similar interaction from C-9, suggesting a reason for the lower sensitivity of the reaction towards substituent effects from this more distant position.



(1)



(2)

Computational Method.—Optimised geometries and heats of formation of the series of substituted anthracenes and of their derived chloroanthracenium ions were calculated by the MNDO computer program package implemented on the CDC 7600 computer of the University of London. Self-consistent field LCAO-MO calculations were carried out within the semi-empirical NDDO approximation,[18–23] since this method provided the best balance between computational accuracy and the size of the system. In particular, this program has been shown to model Cl reasonably well.[24] All calculations were of a closed-shell spin-restricted (RHF) type. Geometry optimisation was performed by a modified Davidon–Fletcher–Powell gradient method. A geometry optimisation was performed on anthracene and on the derived σ-complex [10-chloro-9,10-dihydro-9-anthrylium ion (1)] to maintain the symmetry of the molecules [D_{2h} and the mirror plane C(9)–C(10), respectively]. The energies and geometries were only slightly different from those found when the C–H bond lengths and angles in the outer rings were kept constant, and so this approximation was used to save computing time. A full optimisation was carried out on the 10-chloro-9,10-dihydro-9-nitro-9-anthrylium ion; 78 parameters were allowed to vary, and the final geometry and energy were very close to those found with the more restricted optimisation used on the majority of systems. In particular, the planarity of the outer rings was confirmed, and this feature, together with the carbon–hydrogen bond lengths and angles, was maintained in the majority of calculations.

The starting geometry of the anthracene molecule was taken

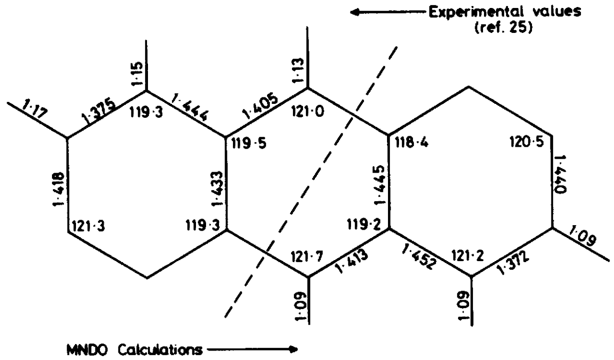


Figure 1. Ground-state anthracene

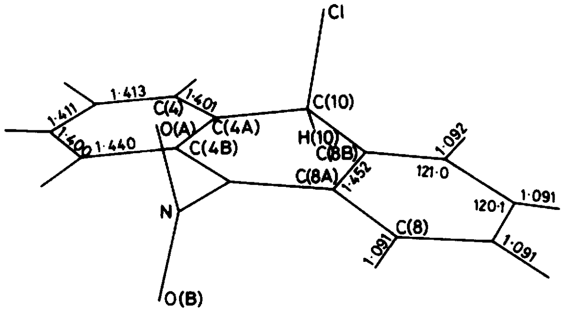


Figure 2. Calculated optimised geometry of 10-chloro-9,10-dihydro-9-nitro-9-anthrylium ion (1)

Table 4. Optimised geometry of 10-chloro-9,10-dihydro-9-nitro-9-anthrylium ion (1)

Bond lengths of middle ring (Å)

C(4A)–C(4B)	1.449	C(10)–C(8B)	1.426
C(8A)–C(8B)	1.452	C(9)–N	1.527
C(4B)–C(9)	1.426	N–O	1.207
C(9)–C(8A)	1.527	C(10)–Cl	1.811
C(4A)–C(10)	1.514	C(10)–H(10)	1.116

Bond angles (°)

C(9)–C(8A)–C(8B)	118.9	C(8B)–C(10)–Cl	107.3
C(8A)–C(8B)–C(10)	119.5	C(4A)–C(10)–H(10)	109.4
C(8B)–C(10)–C(4A)	116.8	O–N–O	123.8
C(8A)–C(9)–C(4B)	124.4		

Torsion angles (°)[a]

C(10)–C(8B),C(8A),C(8)	11.2	N–C(9),C(8A),C(8B)	8.2
C(9)–C(4B),C(4A),C(4)	10.8	C(9)–N,O(A),O(B)	90.6

[a] Quoted as A–B,C,D = angle between atom A and plane BCD.

from results of crystallographic studies by Mason.[25] The optimisation of the energy of the 10-chloro-9,10-dihydro-9-anthrylium ion was begun both from a flat geometry, with the atoms attached to C-10 located above and below the plane, and from the bent geometry of 9,10-dihydroanthracene.[26] In each case, the optimisation converged upon the same final geometry. Calculations involving the substituted anthracenes and their derived ions were begun from a structure using the corresponding geometries and literature values for the bond lengths and angles within the substituents themselves. Alternative calculations were made for each σ-complex in which the chlorine atom was in the *exo*- or the *endo*-configuration; in each case the *exo*-configuration was found to provide the lower energy (Figure 2).

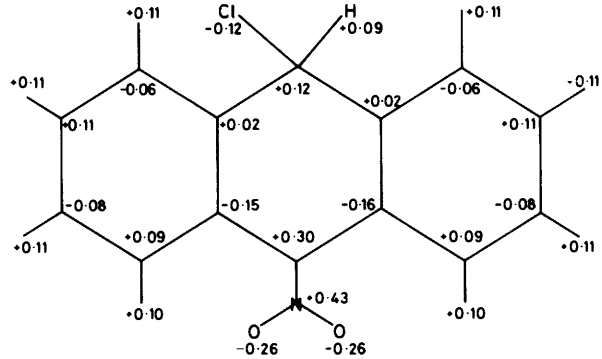


Figure 3. Calculated charge densities in 10-chloro-9,10-dihydro-9-nitro-9-anthrylium ion (1)

From these calculations a number of deductions were possible. The first is the near-agreement between calculated and observed geometries of anthracene (Figure 1). Figure 2 and Table 4 show the optimised geometry of the 10-chloro-9,10-dihydro-9-nitro-9-anthrylium ion (**1**; X = NO_2). In this, the geometry was allowed to vary freely; the minimum energy corresponded to a twist of 0.7° between the planes of the outer rings. Such a small value suggested that it would be appropriate to ignore this option, with the consequent simplification of the computing. Thirdly, the interplanar angles (θ) for the various anthrylium ions (**1**) were found to be 170.8° (X = H), 178.4° (X = OMe), 162.4° (X = Me), 165.7° (X = Cl), 168.3° (X = CHO), and 167.4° (X = CN) when no degree of twist was allowed. The angle between the rings of 9,10-dihydroanthracene is 145°.[23] The difference may be a reflection of the conflicting needs of the central (*meso*) carbon atoms to acquire sp^3 geometry and the delocalisation of the charge across the two benzenoid rings.

Figure 3 shows the calculated charge densities upon each atom in the 10-chloro-9,10-dihydro-9-nitro-9-anthrylium ion (**1**; X = NO_2). Simple MO calculations of electron density within such species suggests that 2/7ths of the charge in the anthrylium ion (**1**; X = H) is located upon the *meso* carbon atom C-9, the rest being spread regularly across the alternant system. The similarity between this and the observed electron density distribution shown in Figure 3 shows the success of the present calculation method in reflecting the manner of delocalisation of charge in such ions without preconceived conditions such as those imposed by the simpler MO method or the resonance theory.

Finally, the agreement between the calculated energy of formation of the σ-complex (**1**) from the anthracene precursor and the experimentally derived free energy for substitution by sulphuryl chloride supports the Bell–Eyring–Polyani model, in which the energy of reaction (E_a) is proportional to the difference between the heats of formation of anthracene and its derived σ-complex. Thus, $E_a = A + B\Delta(\Delta H_f)$, where A and B are constants. The numerical values of B from the graph (Figure 4) is 0.2. A low value of B is held to indicate a transition state nearer to the reactants than to the intermediate, for it reflects the relatively small amount of perturbation necessary to achieve the transition state. The ready attack on anthracene supports this interpretation.

Experimental

Anthracene was purified by co-distillation with diethylene glycol, followed by recrystallisation; 9-substituted anthracenes were generally obtained by substitution reactions. The appropriate literature is cited in Table 1. The kinetic studies were followed by measurement of the formation of sulphur

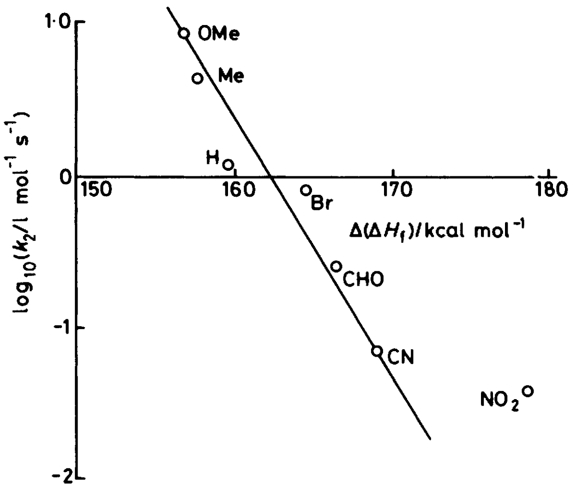


Figure 4. Plot of $\Delta(\Delta H_f)$ *vs.* $\log_{10}$ (k_2/l mol^{-1} s^{-1}) for reactions of SO_2Cl_2 with 9-X-anthracenes

dioxide; details of the experimental method have already been published.[1,10] In all cases, second-order kinetics were demonstrated by doubling the initial concentrations of both sulphuryl chloride and the substituted anthracene; the derived rate constants agreed to within 15% in all cases. Individual rate constants in each kinetic study were consistent to ±5% within each run.

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