

### 237. Application of the Hammett Equation to Cyclopropanes.

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The Hammett equation is shown to be applicable to substituents directly attached to the cyclopropane ring. Data for monosubstituted and 1,1-disubstituted cyclopropanes are apparently best correlated with the  $\sigma_p$  constants, indicating resonance interaction between cyclopropane ring and substituent, comparable to that found in *o*- and *p*-substituted benzene, *cis*- and *trans*-1,2-vinylene, and ethynylene derivatives. Data for *trans*-1,2-disubstituted cyclopropanes are apparently best correlated with the  $\sigma_m$  constants. A possible rationalisation of these results is proposed. Transmission of substituent effects by the cyclopropane ring is discussed.

MANY authors have reported evidence for double-bond character in cyclopropane and its derivatives (a phenomenon not found in other cycloalkanes). The relative ease with which cyclopropanes undergo addition of halogen or hydrogen halide, as compared to other cycloalkanes, suggests some similarity to carbon-carbon double bonds. Of particular interest is the possibility that groups may conjugate with the cyclopropane ring. The possibility of electron delocalisation in the cyclopropane ring has been predicted on theoretical grounds.<sup>1,2</sup> The ultraviolet spectra of cyclopropanes bonded to carbon-carbon double bonds,<sup>3</sup> to carbonyl groups,<sup>4,5</sup> and to aryl<sup>6</sup> and heteroaryl groups<sup>7</sup> show shifts in maxima which are indicative of delocalisation. Studies of infrared spectra,<sup>8</sup> dipole moments,<sup>4,5,9-11</sup> and molar refractivities<sup>12</sup> provide further evidence of significant amounts of conjugation.

Additional evidence for conjugation (or at least of a hybridisation state other than  $sp^3$  for the carbon atoms of the ring) has resulted from studies of molecular dimensions. Petersen, in an X-ray crystallographic study of Feist's acid (*trans*-3-methylenecyclopropane-1,2-dicarboxylic acid), has given a value for the length of the ring-carbon-carbonyl-carbon bond of 1.48 Å.<sup>13</sup> An X-ray crystallographic study of cyclopropane-carboxylic acid hydrazide gave a value for the ring-carbon-carbonyl-carbon bond of 1.48 Å.<sup>14</sup> Friend and Dailey,<sup>15</sup> in an electron-diffraction study of cyclopropyl cyanide, gave a value for the ring-carbon-cyanide-carbon bond of 1.4679 Å. The same authors also examined cyclopropyl chloride and found a carbon-chlorine bond length of 1.7780 Å. All these values are significantly lower than those obtained when the same substituents were attached to  $sp^3$  carbon.

Chemical evidence for conjugation with the carbon-carbon double bond<sup>12</sup> and with the carbonyl group<sup>16</sup> has been reported. In general, the evidence indicates that the

<sup>1</sup> Coulson and Moffitt, *J. Chem. Phys.*, 1947, **15**, 151; *Phil. Mag.*, 1949, **40**, 1; Sugden, *Nature*, 1947, **160**, 367; Walsh, *Nature*, 1947, **159**, 165; *Trans. Faraday Soc.*, 1949, **45**, 179.

<sup>2</sup> Jaffé, *Z. Elektrochem.*, 1959, **59**, 823.

<sup>3</sup> Klotz, *J. Amer. Chem. Soc.*, 1944, **66**, 88.

<sup>4</sup> Roberts and Green, *J. Amer. Chem. Soc.*, 1946, **68**, 214.

<sup>5</sup> Rogers, *J. Amer. Chem. Soc.*, 1947, **69**, 2544.

<sup>6</sup> Robertson, Music, and Matsen, *J. Amer. Chem. Soc.*, 1950, **72**, 5260; Aleksanyan, Sterin, Safonova, Lukina, and Kazanskii, *Optika i Spektroskopiya*, 1959, **7**, 178; Perold, *J.S. African Chem. Inst.*, 1953, **6**, 22.

<sup>7</sup> Mariella, Petersen, and Ferris, *J. Amer. Chem. Soc.*, 1948, **70**, 1494.

<sup>8</sup> Mohrbacher and Cromwell, *J. Amer. Chem. Soc.*, 1957, **79**, 401.

<sup>9</sup> Rogers and Roberts, *J. Amer. Chem. Soc.*, 1946, **68**, 843.

<sup>10</sup> Roberts and Chambers, *J. Amer. Chem. Soc.*, 1951, **73**, 5030.

<sup>11</sup> Spinrad, *J. Amer. Chem. Soc.*, 1946, **68**, 617.

<sup>12</sup> van Volkenburgh, Greenlee, Derfer, and Boord, *J. Amer. Chem. Soc.*, 1949, **71**, 172, 3595.

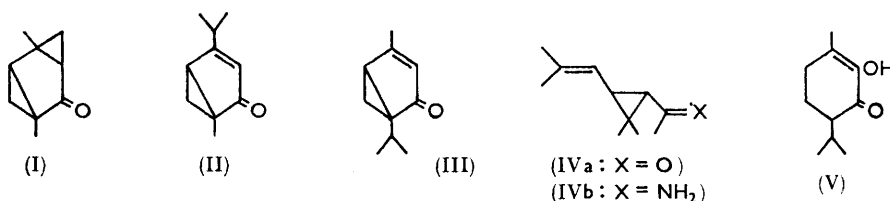
<sup>13</sup> Peterson, *Chem. and Ind.*, 1956, 904.

<sup>14</sup> Chesnut and Marsh, *Acta Cryst.*, 1953, **11**, 413.

<sup>15</sup> Friend and Dailey, *J. Chem. Phys.*, 1953, **29**, 577.

<sup>16</sup> Bone and Perkin, *J.*, 1895, **67**, 108; Kohler and Conant, *J. Amer. Chem. Soc.*, 1917, **39**, 1404; Kierstead, Linstead, and Weedon, *J.*, 1952, 3616.

degree of conjugation of the cyclopropane ring with some  $\pi$ -bonded group such as vinyl, aryl, or carbonyl is less than that of two such groups bonded to each other. Eastman and his co-workers<sup>17</sup> have suggested, on the basis of the ultraviolet spectra of compounds (I), (II), (III), (IVa), and (IVb), and the  $pK_a$  value of (V), that, while a cyclopropane ring may extend a conjugated system, it cannot function as a transmitter of conjugation from one  $\pi$ -bonded group to another. It was pointed out by Mohrbacher and Cromwell<sup>8</sup> that, at least in (I), (II), (III), and (V), steric factors make it impossible for the cyclopropane ring to interact with the carbonyl group. They present evidence from the infrared and ultraviolet spectra for interactions between the phenyl group and the carbonyl group in *trans*-2-phenylcyclopropylcarbonyl compounds. It has recently been noted that interactions between the cyclopropyl group and carbonyl groups are most effective when the cyclopropane ring is parallel to the  $p$  orbitals of the carbonyl groups.<sup>18</sup> Such a situation obviously cannot be realised in (I), (II), (III), and (V). Examination of the Stuart-Briegleb models of (IVa) and (IVb) shows that these substances cannot attain the necessary conformation, owing to steric hindrance. It would seem, therefore, that

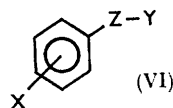


examination of compounds (I)—(V) cannot show whether or not the cyclopropane ring can function as a transmitter of conjugation from one group to another. In addition to Mohrbacher and Cromwell, several other authors have reported conjugation of groups through the cyclopropane ring.<sup>19</sup>

The Hammett equation,<sup>20,21</sup> which may be written in the general form,

$$Q_X = \rho\sigma_X + Q_H, \quad (1)$$

where  $Q$  is the quantity correlated,  $\rho$  the reaction parameter,  $\sigma$  the substituent parameter, and X and H denote the substituted and unsubstituted members of the series, respectively, was first applied to the study of transmission of conjugation through the cyclopropane ring by Trachtenberg and Odian.<sup>22</sup> These authors determined  $\rho$  for the ionisation constants of *trans*-2-(4-substituted phenyl)cyclopropanecarboxylic acids. Jaffé<sup>21</sup> proposed that the variation of  $\rho$  with the side-chain Z in compounds of type (VI), where X is the substituent and Y the reaction site, is indicative of the extent to which Z transmits the substituent effect. Fuchs and Bloomfield<sup>23,24</sup> determined  $\rho$  for the alkaline hydrolysis of ethyl *cis*- and *trans*-2-(3- or 4-substituted phenyl)cyclopropanecarboxylates and of ethyl *cis*- and *trans*-cinnamates. These results, together with those of Fuchs *et al.*,<sup>25</sup> are given in Table 1.



<sup>17</sup> Eastman, *J. Amer. Chem. Soc.*, 1954, **76**, 4115; Eastman and Selaver, *ibid.*, 1954, **76**, 4118; Eastman and Freeman, *ibid.*, 1955, **77**, 6642; Smith and Eastman, *ibid.*, 1957, **79**, 5500.

<sup>18</sup> Kosower and Ito, *Proc. Chem. Soc.*, 1962, 25.

<sup>19</sup> Kierstead, Linstead, and Weedon, *J.*, 1953, 1799; Perold, *J.S. African Chem. Inst.*, 1955, **8**, 1; Cannon, Santilli, and Shenian, *J. Amer. Chem. Soc.*, 1959, **81**, 1660.

<sup>20</sup> Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, 1940.

<sup>21</sup> Jaffé, *Chem. Rev.*, 1953, **53**, 191.

<sup>22</sup> Trachtenberg and Odian, *J. Amer. Chem. Soc.*, 1958, **80**, 4018.

<sup>23</sup> Fuchs and Bloomfield, *J. Amer. Chem. Soc.*, 1959, **81**, 3158.

<sup>24</sup> Bloomfield and Fuchs, *J. Org. Chem.*, 1961, **26**, 2991.

<sup>25</sup> Fuchs, Kaplan, Bloomfield, and Hatch, *J. Org. Chem.*, 1962, **27**, 733.

The  $\rho$  values for alkaline hydrolysis seem to indicate significantly greater transmission through the cyclopropyl group relative to the  $-\text{CH}_2\cdot\text{CH}_2-$  groups.<sup>24</sup> The  $\rho$ -values for the ionisation of the acids have been interpreted by Trachtenberg and Odian to indicate

TABLE I.

Reaction series	$\rho_A$ *	Ref.	$\rho_A$ †	Ref.	$\rho_E$ ‡	Ref.
3-Phenylpropanoic acids ( $Z = \text{CH}_2\cdot\text{CH}_2$ ) .....	0.212	21	0.344	25	0.489	21
	0.204	22				
<i>cis</i> -Cinnamic acids ( $Z = \text{CH}=\text{CH}$ ) .....	0.643	24			1.122	24
<i>trans</i> -Cinnamic acids ( $Z = \text{CH}=\text{CH}$ ) .....	0.466	21			1.314	24
<i>cis</i> -2-Phenylcyclopropanecarboxylic acids .....			0.436	25	1.014	24
<i>trans</i> -2-Phenylcyclopropanecarboxylic acids ...	0.182	22	0.473	25	0.812	23

\* For ionisation in water at 25°. † For ionisation in 50% EtOH-H<sub>2</sub>O at 25°. ‡ For alkaline hydrolysis in 87.8% EtOH-H<sub>2</sub>O at 30°.

that, as the cyclopropane ring is no more effective in the transmission of substituent effects than is the  $-\text{CH}_2\text{CH}_2-$  group, the cyclopropane ring cannot be linking the carboxyl group and the benzene ring by conjugation. The question now arises of whether or not the transmission of the substituent effect, as measured by the  $\rho$ -value, will be proportional to the degree of conjugation of the benzene ring and the carbonyl group through the cyclopropane ring. It has been shown that  $\rho$ -values for reaction series in which resonance does take place can be calculated from an electrostatic equation.<sup>26</sup> These calculations have been made for the ionisation of carboxylic acids and the alkaline hydrolysis of esters. The results for the ionisation of carboxylic acids show that the  $\rho$ -value is dependent on the conformation of the acid. It is entirely possible for the  $\rho$ -value of a series in which resonance occurs to be smaller than the  $\rho$ -value for a series in which no resonance is possible. In view of the uncertainty in interpreting these results, it seemed worthwhile to attempt to study conjugation, both with and through the cyclopropane ring, by another approach.

The Hammett equation has been used to correlate data for vinylene reaction series<sup>27,28</sup> and acetylene reaction series<sup>29</sup> by means of the  $\sigma_p$  constants, and for vinylidene reaction series<sup>30</sup> by means of the  $\sigma_m$  constants.

Taft<sup>31</sup> has suggested that  $\sigma_p$  constants are given by eqn. (2) and  $\sigma_m$  constants by eqn. (3).

$$\sigma_p = \sigma_I + \sigma_R; \quad (2)$$

$$\sigma_m = \sigma_I + 1/3 \sigma_R. \quad (3)$$

Thus, by means of a correlation of data for cyclopropane reaction series (in which the substituent is directly attached to the cyclopropane ring) with the  $\sigma_p$ ,  $\sigma_m$ , and  $\sigma_I$  constants, it should be possible to determine the extent of conjugation with the ring. Another approach to this problem would be the use of the four-parameter equation:

$$Q_X = \rho_I \sigma_I + \rho_R \sigma_R + Q_H. \quad (4)$$

In view of the limited data available, the use of eqn. (4) was considered premature, although it would otherwise have been the preferred method of attack on this problem.

<sup>26</sup> Charton, Abstracts of the 137th Meeting of Amer. Chem. Soc., 1960, p. 62-O; 140th Meeting, 1961, p. 57-T.

<sup>27</sup> Charton and Meislich, *J. Amer. Chem. Soc.*, 1958, **80**, 5940.

<sup>28</sup> Hine and Bailey, *J. Amer. Chem. Soc.*, 1959, **81**, 2075; *J. Org. Chem.*, 1961, **26**, 2098; de la Mare, *J.*, 1960, 3823.

<sup>29</sup> Charton, *J. Org. Chem.*, 1961, **26**, 735.

<sup>30</sup> Charton, Abstracts of the 140th Meeting of the Amer. Chem. Soc., 1961, p. 91-Q.

<sup>31</sup> Taft and Lewis, *J. Amer. Chem. Soc.*, 1958, **80**, 2436; Taft, *J. Phys. Chem.*, 1960, **64**, 1805.

A search of the literature provided data for five reaction series:  $pK_a$  values for *trans*-2-substituted cyclopropanecarboxylic acids in water at 25°;  $pK_a$  values for *trans*-2-substituted 3,3-dimethylcyclopropanecarboxylic acids in 80% Methyl Cellosolve at 25°;  $pK_a$  values for 1-substituted cyclopropanecarboxylic acids in water at 25°; dipole moments of substituted cyclopropanes; and near-infrared absorption maxima of substituted cyclopropanes. The data are given in Table 2. For purposes of comparison, literature values

TABLE 2.

Data for cyclopropane reaction series.

(1) $pK_a$ values for <i>trans</i> -2-substituted cyclopropanecarboxylic acids in water at 25°.									
	X	Ph	Cyclohexyl	CO <sub>2</sub> H	CO <sub>2</sub> <sup>-</sup>	H			
$pK_a$ .....		4.50	4.79 *	3.95 †	4.83 ‡	4.83			
Ref. ....		22	32	33	33	33			
(2) $pK_a$ values for <i>trans</i> -2-substituted 3,3-dimethylcyclopropanecarboxylic acids in 80% Methyl Cellosolve at 25°.									
	X	Bu	Ph	OPr <sup>i</sup>	CO <sub>2</sub> <sup>-</sup>	CO <sub>2</sub> H			
$pK_a$ .....		7.90	7.42	7.55	7.77 §†	6.31			
Ref. ....		32	32	32	33	33			
(3) $pK_a$ values for 1-substituted cyclopropanecarboxylic acids in water at 25°.									
	X	H	Cl	CO <sub>2</sub> H	CO <sub>2</sub> <sup>-</sup>				
$pK_a$ .....		4.83	3.26	2.12 †	5.13 ‡				
Ref. ....		33	34	33	33				
(4) Dipole moments of substituted cyclopropanes.									
	X	Ph	Ac	H	Et	Cl	CN	Pr	Br
$\mu$ (D) .....		0.49	2.84	0	0.18	1.76	3.75	0.75	1.69
Ref. ....		5	5	35	36	9, 10, 11	9	37	10
(5) Near-infrared spectra: wavelengths of cyclopropane absorption (ref. 38).									
	X	CN	CO <sub>2</sub> H	CO <sub>2</sub> Me	Ac	Ph	Et	Bu	
$\lambda$ (microns) .....		1.624	1.626	1.627	1.628	1.635	1.639	1.639	

\* Estimated from value in 80% Methyl Cellosolve at 25°. † Includes a statistical factor of 1/2. ‡ Includes a statistical factor of 2. § Estimated from value in water at 25°. Estimated values were calculated from the linear relation between  $pK_a$ 's in the two solvents, obtained by least mean squares.

of  $pK_a$  for *trans*-2-substituted cyclohexanecarboxylic acids in water at 25° and of the dipole moment for substituted cyclobutanes, cyclopentanes, and cyclohexanes were also correlated with the Hammett equation. The data for these series are given in Table 3.

## RESULTS

*Correlations.*—The correlations were made by the method of Jaffé.<sup>21</sup> Each series was correlated separately with  $\sigma_m$ ,  $\sigma_p$ , and  $\sigma_I$  constants. The  $\sigma_m$  and  $\sigma_p$  constants used were taken, where possible, from the compilation of McDaniel and Brown.<sup>50</sup> The  $\sigma_I$  values used were those of Taft and Lewis,<sup>31</sup> where possible. Values of  $\sigma_m$ ,  $\sigma_p$ , and  $\sigma_I$ , taken from other sources, are given in Table 4. The results of the correlations for the cyclopropane reaction series are given in Table 5, and for the other reaction series in Table 6.

<sup>22</sup> Šmejkal, Jonáš, and Farkaš, *Coll. Czech. Chem. Comm.*, 1960, **25**, 1746.

<sup>23</sup> Kortum, Vogel, and Andrussov, "Dissociation Constants of Organic Acids in Aqueous Solution," Butterworths, London, 1961.

<sup>24</sup> Bruylants and Stassens, *Bull. Classe Sci. Acad. roy. Belg.*, 1921, 702.

<sup>25</sup> Ramaswamy, *Proc. Indian Acad. Sci.*, 1936, **A**, **4**, 108.

<sup>26</sup> vanArkel, Meerburg, and vandenHandel, *Rec. Trav. chim.*, 1942, **61**, 767.

<sup>27</sup> Boeseken and Takes, *Rec. Trav. chim.*, 1937, **56**, 858.

<sup>28</sup> Gassman, *Chem. and Ind.*, 1962, 740.

TABLE 3.

Data for cyclobutane, cyclopentane, and cyclohexane reaction series.

(6)  $pK_a$  values for *trans*-2-substituted cyclohexanecarboxylic acids in water at 25°.

X	H	Me	OH	CN	CO <sub>2</sub> H	CO <sub>2</sub> <sup>-</sup>	MeO
$pK_a$ .....	4.900	5.735	4.682	3.8649	4.481 *†	5.627 †§	4.79 ¶
Ref. ....	33	33	33	33	33	33	39

(7) Dipole moments of substituted cyclobutanes.

X	H	CO <sub>2</sub> H	Br	CO <sub>2</sub> Me	Et	CN
$\mu$ (D) .....	0.00	1.60	2.09	1.96	0.05	3.48
Ref. ....	40	41	10	41	36	41

(8) Dipole moments of substituted cyclopentanes.

X	H	F	Me	Cl	Br	I	CN	CO <sub>2</sub> Me	CO <sub>2</sub> Et
$\mu$ (D) .....	0.00	1.86	0.00	2.08	2.20	2.06	3.71	1.63	1.28
Ref. ....	36	9	36	9	9	9	9	42	42

(9) Dipole moments of substituted cyclohexanes.

X	H	Cl	Br	I	Me	E	Pr <sup>1</sup>
$\mu$ .....	0	2.3	2.31	1.98	0	0	0
Ref. ....	43	43, 44	10	44	45	45	45

X	Bu <sup>t</sup>	OH	SH	CO <sub>2</sub> Me	CO <sub>2</sub> Et	CF <sub>3</sub>	OMe
$\mu$ (D) .....	0	1.82	1.73	1.40	1.27	2.40	1.35
Ref. ....	45	46	47	42	42	48	49

\* Includes statistical factor of 1/2. † At 18°. ‡ Includes statistical factor of 2. § At 19°. ¶ Estimated from  $pK_a$  in 80% aqueous Methyl Cellosolve. See Table 2, footnote §.

TABLE 4.

Substituent constants obtained from sources other than refs. 31 and 50.

Substituent	CO <sub>2</sub> Me	CN	Pr	Pr <sup>1</sup>	Bu <sup>t</sup>	OPr <sup>1</sup>	CO <sub>2</sub> <sup>-</sup>	Cyclohexyl
$\sigma_m$ .....	—	0.615 <sup>51</sup>	-0.05*	-0.07*	-0.07*	—	—	-0.06§
$\sigma_p$ .....	0.436 <sup>27</sup>	—	—	—	—	-0.286 <sup>21</sup>	—	-0.15¶
$\sigma_I$ .....	—	—	-0.02†	0.03†	-0.05†	0.29†	-0.15‡	-0.05

\* Calculated from  $\sigma_m = (\sigma_p + 2\sigma_I)/3$ . † Calculated from  $\sigma_I = \sigma^*/6.23$ . ‡ Calculated from  $\sigma_I = (3\sigma_m - \sigma_p)/2$ . § Assumed equal to  $\sigma_m^+$  for Pr<sup>1</sup>, given by ref. 52. ¶ Assumed equal to  $\sigma_p$  for Pr<sup>1</sup>. || Assumed equal to  $\sigma_I$  for Et.

*Ionisation Constants.*—The  $pK_a$  values used were in some cases calculated from values in other solvent systems by means of the linear relationship between the values in the two systems. The necessary linear relationships were obtained from data in the literature by least-mean-squares. Statistical factors of 1/2 and 2 were used for the values of  $pK_{a1}$  and  $pK_{a2}$ , respectively, of dicarboxylic acids. The results for the *trans*-2-substituted cyclopropanecarboxylic acids (Series 1), and to an even greater extent for the *trans*-2-substituted 3,3-dimethylcyclopropanecarboxylic acids (Series 2), show best correlation

<sup>39</sup> Febrer and Pascual, *Anales real Soc. españ. Fis. Quim.*, 1956, **52**, 541.

<sup>40</sup> Smyth, "Dielectric Constant and Structure," McGraw-Hill, New York, 1955.

<sup>41</sup> Nevill, Frank, and Taylor, *J. Org. Chem.*, 1962, **27**, 422.

<sup>42</sup> Mousseron, *Bull. Soc. chim. France*, 1947, 605.

<sup>43</sup> Williams, *J. Amer. Chem. Soc.*, 1939, **52**, 1831.

<sup>44</sup> Hassel and Naeshagen, *Z. phys. Chem.*, 1932, **B**, **15**, 373.

<sup>45</sup> Baker and Groves, *J.*, 1939, 1144.

<sup>46</sup> Halverstadt and Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 1982.

<sup>47</sup> Mathias, de Carvalho-Filho, and Cecchini, *J. Phys. Chem.*, 1961, **65**, 425.

<sup>48</sup> Roberts, Webb, and McElhill, *J. Amer. Chem. Soc.*, 1950, **72**, 408.

<sup>49</sup> Groves and Sugden, *J.*, 1937, 1779.

<sup>50</sup> McDaniel and Brown, *J. Org. Chem.*, 1958, **23**, 420.

<sup>51</sup> Fickling, Fischer, Mann, Packer, and Vaughan, *J. Amer. Chem. Soc.*, 1959, **81**, 4226.

<sup>52</sup> Okamoto and Brown, *J. Org. Chem.*, 1957, **22**, 485.

TABLE 5.  
 Cyclopropane reaction series.

Series	$\rho_m$	$\rho_p$	$\rho_I$	$r^*$	$s^\dagger$	$t^\ddagger$	$Q_H$ (calc.)	$n^\S$
1	-1.975 ¶	-1.509	-2.018	0.975	0.972	7.582	4.69	5
				0.910	0.181	3.801	4.63	
				0.931	0.160	4.415	4.616	
2	-3.294	-1.987	-2.377	0.964	0.195	6.259	7.63	5
				0.857	0.375	2.882	7.41	
				0.733	0.496	1.866	7.60	
3	-5.357	-6.470	-4.126	0.939	0.590	3.878	4.70	4
				0.991	0.225	10.76	4.93	
				0.825	0.975	2.062	4.47	
4	5.914	5.274	5.576	0.964	0.454	8.859	-0.0517	8
				0.985	0.289	14.22	0.32	
				0.887	0.787	4.708	-0.604	
5	-0.0224	-0.0190	-0.0274	0.972	0.00164	9.239	1.636	7
				0.978	0.00146	10.49	1.636	
				0.947	0.00225	6.586	1.637	

\* Correlation coefficient. † Standard deviation. ‡ "Student"  $t$  test for the significance of  $\rho$ :  $t = \rho/S_\rho$ . § Number of compounds in the series. ¶ The - signs on the  $\rho$ -values are due to the correlations' having been made directly with  $pK_a$  values. For comparison with the  $\rho$ -values given in Ref. 21 for ionisation of series of acids or bases, signs should be changed to +.

TABLE 6.

Cyclobutane, cyclopentane, and cyclohexane reaction series.\*\*

Series	$\rho_m$	$\rho_p$	$\rho_I$	$r^*$	$s^\dagger$	$t^\ddagger$	$Q_H$ (calc.)	$n^\S$
6	-2.322	-1.036	-2.442	0.924	0.272	5.387	5.217	6
				0.606	0.565	1.702	4.919	
				0.944	0.234	6.401	5.28	
7	5.162	4.046	5.373	0.985	0.259	11.52	0.13	6
				0.927	0.569	4.925	0.44	
				0.981	0.292	10.18	0.11	
8	5.470	4.666	4.817	0.960	0.345	9.027	0.0732	9
				0.780	0.767	3.301	0.80	
				0.931	0.448	6.735	0.059	
9	4.390	4.082	4.617	0.914	0.413	7.779	0.43	14
				0.878	0.684	6.358	0.44	
				0.972	0.237	14.43	0.25	

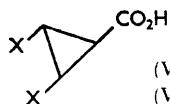
\*\* For footnotes see Table 5.

with the  $\sigma_m$  constants. Recently, values for the ionisation constants of *trans*-2,3-diphenyl- and *trans*-2,3-dipropyl-cyclopropanecarboxylic acids (VIIa and VIIb) in 50% aqueous ethanol have been reported.<sup>53</sup>

The  $pK_a$  values for water were calculated from the ionisation constants of the acids, and have been included in series 1 by using the equation:

$$Q_X = \rho \sum \sigma_X + Q_H, \quad (1a)$$

where  $\sum \sigma_X$  is the sum of the  $\sigma$  constants for groups in the 2- and 3-position. Results of the correlation of this extended series are shown in Table 7; they seem to indicate a definitely superior correlation with  $\sigma_m$ , as compared to that with  $\sigma_I$  or  $\sigma_p$ .



$$pK_a, \text{H}_2\text{O} = 4.51$$

$$\text{(VIIa: X = Ph)} \quad pK_a, \text{H}_2\text{O} = 5.04$$

$$\text{(VIIb: X = Pr)}$$

The results for the *trans*-2-substituted-cyclohexanecarboxylic acids (Series 6) show best correlation with the  $\sigma_I$  constants. This correlation is improved by dropping the value for

<sup>53</sup> D'yaKonov, Komendatov, Fu, and Korichev, *J. Gen. Chem. (U.S.S.R.)*, 1962, **32**, 917.

the unsubstituted acid ( $X = H$ ) from the series. This is probably due to the fact that the other acids in the series are largely in the  $e,e$  conformation, whereas the unsubstituted acid may exist in the  $a$  conformation to a greater extent. It is particularly significant that correlation for series 1 and 2 with the  $\sigma_p$  constants, while poor, is very much greater than that of series 6. This is further evidence for some degree of resonance interaction in series 1 and 2. Series 3 is best correlated by  $\sigma_p$ .

*Dipole Moments.*—The successful correlation of the dipole moments of substituted benzenes,<sup>53</sup> acetylenes,<sup>29</sup> and olefins<sup>54</sup> suggested the possibility of correlating the dipole moments of cyclopropanes. In these correlations, minus signs were assigned to those groups (except phenyl) whose  $\sigma$  constants are negative. In the case of the phenyl group, the  $\sigma_p$  constant has a negative sign, but is not significantly different from zero. The results show that the substituted cyclopropanes (Series 4) are best correlated by the  $\sigma_p$  constants. Although the correlation coefficient for correlation with the  $\sigma_m$  constants is good, the value of  $t$  shows that better correlation is obtained with  $\sigma_p$ . The dipole moments of substituted cyclobutanes show about equally good correlation with  $\sigma_m$  and  $\sigma_I$ . The dipole moments of substituted cyclopentanes show good correlation with  $\sigma_m$ , fair correlation with  $\sigma_I$ , and poor correlation with  $\sigma_p$ . This is surprising, but it should be noted that this series encompasses the smallest range of substituent types (H, alkyl, cyano, halogen, alkoxy-carbonyl) of all the series studied. The cyclohexanes give best correlation with  $\sigma_I$ .

TABLE 7.  
Cyclopropane reaction series correlated with eqn. 1a.\*\*

Series	$\rho_m$	$\rho_p$	$\rho_I$	$r^*$	$s^\dagger$	$t^\ddagger$	$n^\S$
1a	-2.053	-1.487	-1.953	0.974	0.0895	9.526	7
				0.913	0.260	4.994	
				0.883	0.184	4.207	
5a	-0.0194	-0.0189	-0.0158	0.936	0.00239	6.492	8
				0.980	0.00135	12.10	
				0.824	0.00384	3.563	
5b	-0.0241	-0.0234	-0.0211	0.933	0.00338	6.861	9
				0.944	0.00310	7.568	
				0.840	0.00511	4.091	

\*\* For footnotes see Table 5.

*Near-infrared Absorption Spectra of Substituted Cyclopropanes.*—The correlation coefficients show good correlation with  $\sigma_m$  and  $\sigma_p$ , and fair correlation with  $\sigma_I$ . The standard deviations, however, indicate that best correlation is with the  $\sigma_p$  constants.

If the value ( $\lambda = 1.625$  microns) for 1,1-dichlorocyclopropane is included in the series, and  $\Sigma\sigma$  is used in the correlation, the results indicate far better correlation with  $\sigma_p$  (Series 5a, Table 7). Further inclusion of the value ( $\lambda = 1.650$  microns) for 1,1,2,2-tetramethylcyclopropane, and use of  $\Sigma\sigma$ , gives good correlation with  $\sigma_p$  and  $\sigma_m$  but poor correlation with  $\sigma_I$  (Series 5b, Table 7). This change in correlation with  $\sigma_p$ , relative to  $\sigma_m$ , is not unexpected. In series 5 and 5a, substituents are attached only to C-1. Inclusion of 1,1,2,2-tetramethylcyclopropane involves substitution at both C-1 and C-2.

## DISCUSSION

*Conjugation in Cyclopropane Systems.*—Of the *trans*-2-substituted cyclopropane series studied, series 1 gave the correlation order  $\sigma_m > \sigma_I > \sigma_p$ , series 1a gave  $\sigma_m \gg \sigma_p > \sigma_I$ , and series 2 gave  $\sigma_m \gg \sigma_p \gg \sigma_I$ . This suggests that the resonance contribution,  $\sigma_R$ , in these series is approximately equal to 1/3 of that found in a substituent bonded to *o*- or *p*-phenylene, *cis*- or *trans*-vinylene, or ethynylene groups.

Of the 1-substituted cyclopropanes series studied, series 3 gave the correlation order

<sup>54</sup> Charton, Abstracts of the 141st Meeting of the Amer. Chem. Soc., 1962, p. 47-R.

1212 *Application of the Hammett Equation to Cyclopropanes.*

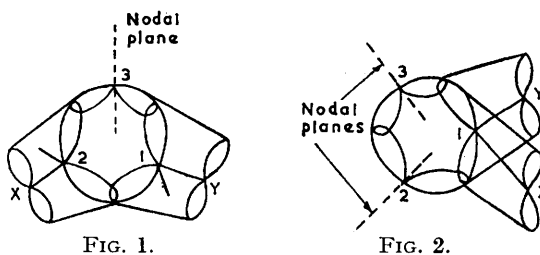
$\sigma_p \gg \sigma_m \gg \sigma_I$ , series 4 gave  $\sigma_p \gg \sigma_m \gg \sigma_I$ , series 5 gave  $\sigma_p > \sigma_m > \sigma_I$ , and series 5a gave  $\sigma_p \gg \sigma_m \gg \sigma_I$ . These results indicate a  $\sigma_R$  contribution to substituents in these series of about the same magnitude as that found in a substituent attached to *o*- or *p*-phenylene, *cis*- or *trans*-vinylene, or ethynylene groups.

These results may be rationalised as follows. Both lobes of the *p* or  $\pi$  orbitals of a substituent in the 2-position cannot overlap the *endo* ring orbitals<sup>55</sup> and the *p* or  $\pi$  orbitals of the reaction site (Fig. 1). A nodal plane must pass through C-3 and one lobe of the  $\pi$  orbital. In the 1-position, however, both lobes of the *p* or  $\pi$  orbitals of the substituent and reaction site are capable of overlap with the *endo* orbitals of C-1 in the ring. In Fig. 2, the nodal planes through C-2 and C-3 prevent overlap with the *endo* C-2-C-3 bond. This argument is implicit in Jaffé's discussion of bonding in the cyclopropane ring.<sup>2</sup>

*Transmission of Substituent Effects by the Cyclopropane Group.*—A comparison of the transmission of substituent effects through various systems may be made by use of eqn. (5):

$$\gamma = \rho_G/\rho_{G^\circ} \quad (5)$$

where  $\rho_G$  is the reaction constant for the group G being considered and  $\rho_{G^\circ}$  is the reaction constant for a standard group  $G^\circ$ . Transmission of substituent effects may also be compared by means of the  $\tau$ -values proposed by Hine.<sup>56</sup> Values of  $\gamma$  and  $\tau$  are given in Table 8.



FIGS. 1 and 2. Overlap of orbitals in substituted cyclopropanes.

The  $\tau$ -values quoted in Table 8 for the *m*- and *p*-phenylene groups are those obtained by Hine<sup>56</sup> from the ionisation of benzoic acids, rather than the average values which he reports. The  $\tau$ -value for series 1 was calculated from  $\rho_m$ , and that for series 3 from  $\rho_p$ .

TABLE 8.

Transmission of substituent effects.

Group	$\gamma$	$\tau$	Group	$\gamma$	$\tau$
<i>p</i> -Phenylene .....	1.00 *	3.05 †	Ferrocenylene .....	0.677	2.4 ‡
<i>trans</i> -Vinylene .....	2.23	6.52 ‡	<i>trans</i> -Cyclopropylene ...	1.98	4.43
<i>m</i> -Phenylene .....	1.00 *	2.66	Cyclopropylidene .....	5.36	0.53
Ethynylene.....	1.89	5.13 ‡			

\*  $\rho_{G^\circ}$  is for ionisation of benzoic acids in water at 25°. † Ref. 56. ‡ Ref. 29.

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<sup>55</sup> Ingraham, "Steric Effects in Organic Chemistry," Wiley, New York, 1956.

<sup>56</sup> Hine, *J. Amer. Chem. Soc.*, 1959, **81**, 1126.