Comparison of Field and σ-Inductive Models for the Transmission of Nonconjugative Substituent Effects. The 2,6-Spiro[3,3]heptyl System

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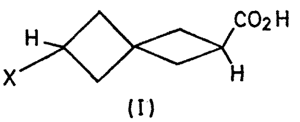
Summary The pK_a values of a series of 6-substituted spiro[3,3]heptane-2-carboxylic acids have been measured in 50% (by wt.) aqueous ethanol and the results analysed in terms of the mechanism of transmission of nonconjugative substituent effects.

A series of 6-substituted spiro[3,3]heptane-2-carboxylic acids (I) have been synthesized and their pK_a values determined in 50% (by weight) aqueous ethanol at 25°. The results are summarized in Table 1.

In order to explore the question of which model, field or σ-inductive,[1] most adequately described the transmission of nonconjugative substituent effects, a graphical comparison was made between the pK_a values of series (I) and the pK_a

values of the corresponding 4-substituted bicyclo[2,2,2]-octane-1-carboxylic acids (series II) in 50% (by weight) aqueous ethanol at 25° (Figure).[2] An excellent linear correlation was obtained with a slope equal to 2·04. We wished to make a similar comparison between series (I) and the 4-substituted bicyclo[2,2,1]heptane-1-carboxylic acids (series III). Unfortunately, the pK_a values of series (III) in 50% (by weight) aqueous ethanol have not been reported. Wilcox and Leung,[3] however, have compared the relative acidities of series (II) and (III) in pure water, 25% methanol–water, and 50% methanol–water and have obtained ρ values of 1·175, 1·183, and 1·195, repsectively. A plot of ρ against $1/D$ produces a straight line,[4] which, when extrapolated to the $1/D$ value for 50% (by weight) aqueous ethanol (D = 49·5) gives a ρ value of 1·210. The "experimental" slope in the comparison of series (I) and (III) is then calculated to be 2·44. In order to evaluate the theoretical slopes from the σ-inductive model, attenuation factors of 1/2·0 and 1/3·0[5] were used (see equations 1 and 2).

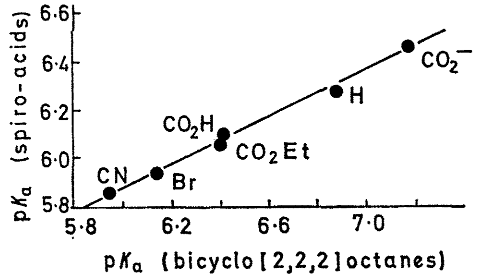
TABLE 1



(I)

X	pK_a
H	6·266 ± 0·015
Br	5·931 ± 0·015
CN	5·856 ± 0·018
CO_2Et	6·062 ± 0·025
CO_2H[a]	6·088 ± 0·015
CO_2^-[a]	6·406 ± 0·032

[a] Statistically corrected.



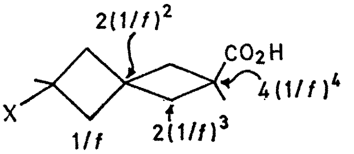
FIGURE

$$\text{Ratio of (II) to (I)} = 3(1/f)^3/4(1/f)^4 = 3f/4 \qquad (1)$$

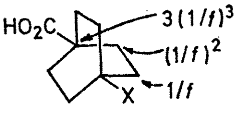
$$\text{Ratio of (III) to (I)} = [2(1/f)^3 + (1/f)^2]/4(1/f)^4 = [2f + f^2]/4 \qquad (2)$$

The theoretical slopes for the field model were evaluated by means of the Tanford modification of the Kirkwood–Westheimer spherical cavity model.[6] The results are summarized in Table 2.

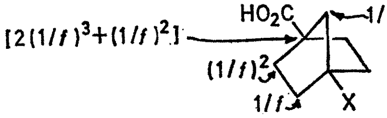
It can be seen that the slopes predicted by the field model and the experimental slopes are almost identical, whereas the slopes predicted by the σ-inductive model cover an extremely wide range. Wilcox and Leung[3] have suggested that an attenuation factor of 1/2·7 is most reasonable. Using this value, the predicted σ-inductive slopes becomes almost identical to both the experimental and field slopes in the comparison of series (I) and (II). This same attenuation factor, however, predicts a slope for series (I) and (III) which is far from the field and experimental slopes. These results suggest that the field model is superior to the σ-inductive model in predicting the relative magnitude of nonconjugative substituent effects.



(I)



(II)



(III)

TABLE 2

Experimental and theoretical ρ-values in the comparison of spiro-[3,3]*heptane* (I), *Bicyclo*[2,2,2]*octane* (II), *and bicyclo*[2,2,1]-*heptane acids* (III).

	I–II	I–III
Slope, ρ (exp.)	2·04	2·44
Slope, ρ (TMKW)	2·03	2·40
Slope, ρ (inductive) $1/f$ = 1/2–1/3	1·50—2·50	2·00—3·75
Slope, ρ (inductive) $1/f$ = 1/2·7	2·02	3·17

We thank the National Science Foundation and the Petroleum Research Foundation for support of this work.

(*Received, July 28th,* 1969; *Com.* 1145.)

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[1] M. J. S. Dewar and J. Grisdale, *J. Amer. Chem. Soc.*, 1962, **84**, 3539, 3548.

[2] H. D. Holtz and L. M. Stock, *J. Amer. Chem. Soc.*, 1964, **86**, 5188; F. W. Baker, R. C. Parish, and L. M. Stock, *ibid.*, 1967, **89**, 5677.

[3] C. F. Wilcox and C. Leung, *J. Amer. Chem. Soc.*, 1968, **90**, 336.

[4] K. B. Wiberg, "Physical Organic Chemistry," Wiley, New York, 1964, pp. 259—260.

[5] R. W. Taft, jun., "Steric Effects in Organic Chemistry," ed. M. S. Newmann, Wiley, New York, 1955, ch. 13; J. C. McGowan, *J. Appl. Chem.*, 1960, **10**, 312; B. M. Wepster, *Rec. Trav. chim.* 1952, **71**, 1171; G. W. Stevenson and D. Williamson, *J. Amer. Chem. Soc.*, 1958, **80**, 5943.

[6] C. Tanford, *J. Amer. Chem. Soc.*, 1957, **79**, 5348; J. G. Kirkwood and F. H. Westheimer, *J. Chem. Phys.*, 1938, **6**, 506; F. H. Westheimer and J. G. Kirkwood, *ibid.*, p. 513; F. H. Westheimer and M. W. Shookhoff, *J. Amer. Chem. Soc.*, 1939, **61**, 555; F. H. Westheimer, W. A. Jones, and R. A. Lad, *J. Chem. Phys.*, 1942, **10**, 478.