Curie point. In the present case, however, different magnetic states of the catalyst have no effect on the reaction. The same deduction can be drawn as to the reversal of the temperature coefficient of the resistivity of the catalyst. On the other hand, the data of Fig. 3 show that in the neighborhood of the ferromagnetic transition an anomaly is present in the rate of the catalytic reaction. This is in agreement with previous findings of Forestier and Lille,[5] who reported anomalies in the rate of the reaction $CO_2 + H_2 \rightleftarrows CO + H_2$ on Fe_3O_4, $SrFe_2O_4$, $NiFe_2O_4$ around the Curie temperature of the catalyst. The anomalous behavior of the activity of a catalytic reaction reported in the present communication is quite similar to that previously found for ferroelectric transitions occurring in sodium and potassium niobate and lanthanum ferrite.[6] It is interesting to note that the anomaly sets in somewhat below the Curie temperature. This could be explained by assuming that the ferromagnetic transition occurs on the surface at a lower temperature than in the bulk.

(5) H. Forestier and R. Lille, *Compt. rend.*, **204**, 265 (1937).

(6) G. Parravano, *J. Chem. Phys.*, **20**, 342 (1952).

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Energy Relationships of Fused Ring Systems

BY WILLIAM S. JOHNSON

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Using the Pitzer parameters[1] of 3.6 kcal. for the eclipsed, and 0.8 kcal. for the skew conformation (the staggered arrangement being set at zero) of the *n*-butane portion of a hydrocarbon chain, Turner[2] has calculated the difference in energy between the *cis* and *trans* forms of decalin to be 2.4 kcal., which, after correction for heats of vaporization, is in excellent agreement with the experimental observation. A simple method of carrying out the calculation of energy difference is as follows:

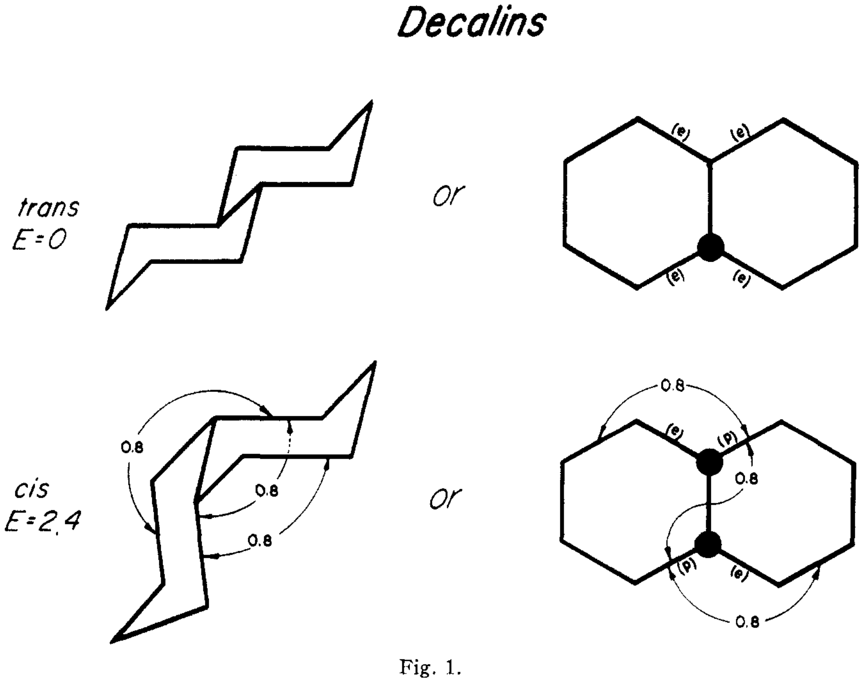

Fig. 1.

trans-Decalin is arbitrarily assigned the value zero; now *cis*-decalin differs from the *trans* isomer only in the three *skew* interactions involving the two polar (p) bonds as shown in Fig. 1. The energy difference, hence, is 3 × 0.8 = 2.4 kcal.

Applied to the perhydro-phenanthrenes and -anthracenes, this method of estimating energy differences leads to a more definitive picture of the relationships that were established qualitatively earlier,[3] and provides a criterion for establishing a more precise order of stability. In addition, this treatment affords an interrelation of the members of the phenanthrene and of the anthracene series on the same energy basis. It should be emphasized, however, that all of these energy differences are for the vapor phase at 25°, and small corrections would be expected[2] for the differences in heats of vaporization of the isomers.

The perhydroanthracenes (see Fig. 2) are conveniently considered first. Since the *trans–syn–trans* is the isomer of lowest energy, it is arbitrarily assigned the value zero. The *cis–syn–trans* form then differs from the *trans–syn–trans* by 3 *skew* interactions or 2.4 kcal. just as in the decalin series considered above. In the *cis–anti–cis* isomer an additional *cis*-decalin fusion is imposed which simply doubles the energy difference, *i.e.*, 6 *skew* interactions = 4.8 kcal.

The *trans–anti–trans* isomer differs from the *trans–syn–trans* in that the central ring assumes the boat conformation,[3] which accounts for a difference in energy of 5.6 kcal., namely, the difference between the chair and boat form of cyclohexane. In addition the *trans–anti–trans* form has two interactions (magnitude uncertain) of the type discussed by Turner,[4] which is defined by a rotation of 60° from the staggered conformation. The total energy difference for this isomer, hence, is a value somewhat greater than 5.6 kcal. In the *cis–syn–cis* isomer the situation is complicated by the fact that two of the (p) bonds appear in the unfavorable 1,3-relationship on the central cyclohexane ring. This interaction is comparable to that of the (p) (p) form of *cis*-1,3-dimethylcyclohexane for which Pitzer[1] has arbitrarily assigned the energy difference of 5.4 kcal. In the present case the interaction of two methylene groups is estimated to be about 8/9 (*skew* methylene/methyl) of this value or 4.8 kcal. With this

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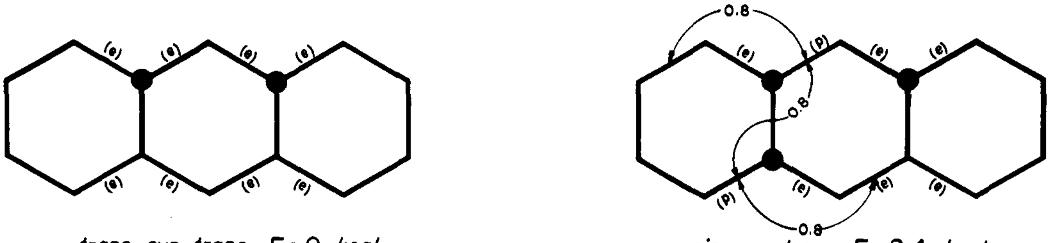
(1) (a) K. S. Pitzer, *Chem. Revs.*, **27**, 39 (1940); (b) C. W. Beckett, K. S. Pitzer and R. Spitzer, THIS JOURNAL, **69**, 2488 (1947).

(2) R. B. Turner, *ibid.*, **74**, 2118 (1952).

(3) W. S. Johnson, *Experientia*, **8**, 315 (1951).

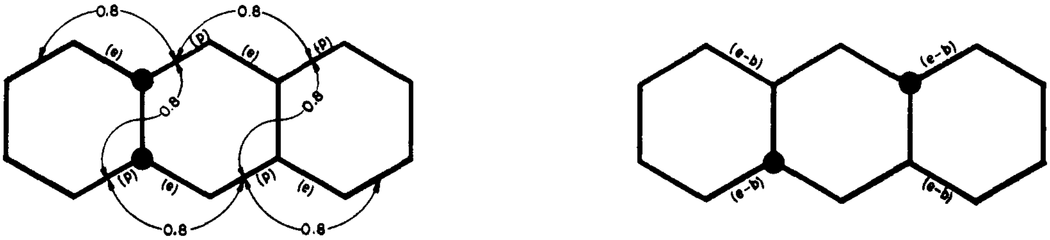
(4) See formula IX, ref. 2.

Perhydroanthracenes



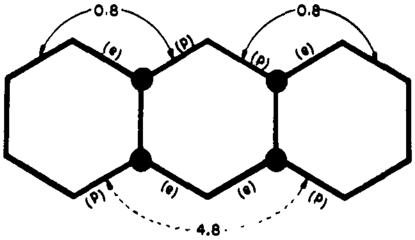
trans-syn-trans, E = 0 *kcal.*

cis-syn-trans, E = 2.4 *kcal.*
(trans-anti-cis)



cis-anti-cis, E = 4.8 *kcal.*

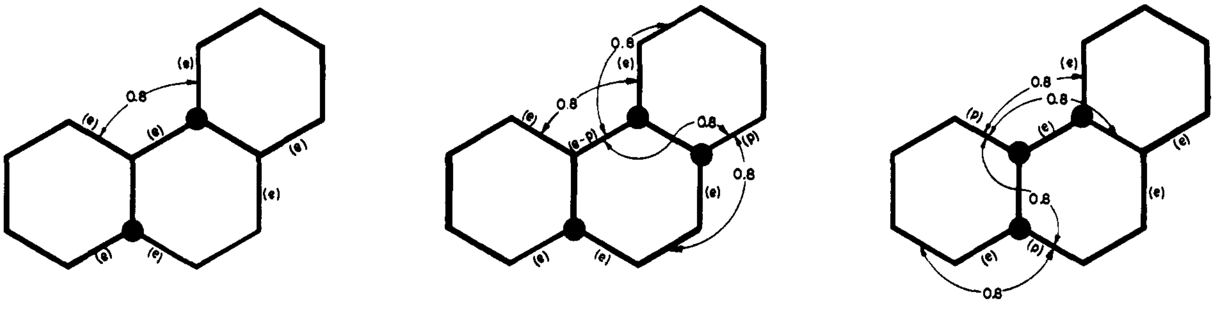
trans-anti-trans, E>5.6 *kcal.*



cis-syn-cis, E = ca. 6.4 *kcal.*

Fig. 2.

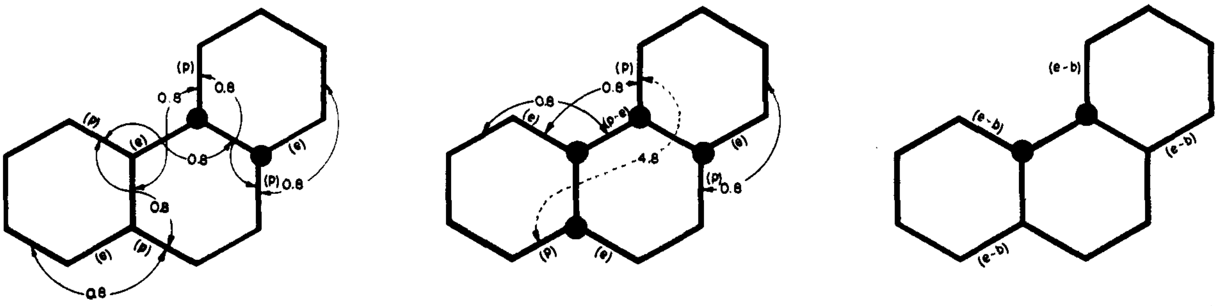
Perhydrophenanthrenes



trans-anti-trans, E = 0.8 *kcal.*

trans-anti-cis, E = 3.2 *kcal.*

cis-syn-trans, E = 3.2 *kcal.*



cis-anti-cis, E = 4.8 *kcal.*

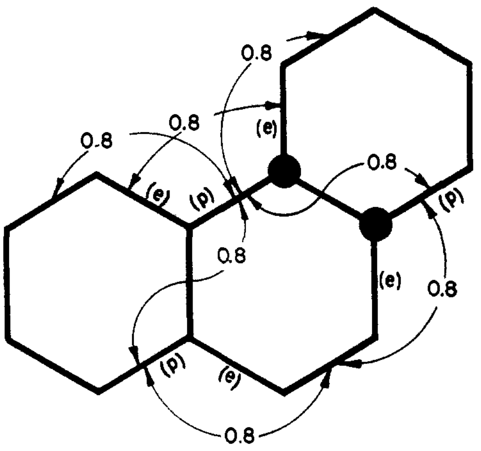
cis-syn-cis, E = ca. 7.2 *kcal.*

trans-syn-trans, E = >5.6 *kcal.*

Fig. 3.

parameter, the energy differences for the *cis–syn–cis* isomer becomes *ca.* 2 × 0.8 + 4.8 = 6.4 kcal.

The most stable of the perhydrophenanthrenes, the *trans–anti–trans* isomer, differs from the *trans–syn–trans* perhydroanthracene by one *skew* interaction between the bonds forming the angle of the three rings, or by 0.8 kcal. (see Fig. 3). The *trans–anti–cis* and *cis–syn–trans* isomers both have one additional *cis*-decalin interaction making the total energy difference 3.2 kcal. The case of the *cis–anti–cis* isomer is of particular interest since the earlier method of analysis[3] did not distinguish between the form with 1,2-(p) (p) substituents on the central cyclohexane ring (as shown in Fig. 3) and the form with 1,4-(p) (p) substituents (Fig. 4).



cis-anti-cis, E = 5.6 *kcal.*

Fig. 4.

In the former the angular skew interaction is eliminated, and the energy difference is defined simply by two *cis*-decalin interactions, or 4.8 kcal. just as in the *cis–anti–cis*-perhydroanthracene. In the latter conformation, the angular *skew* interaction is operative producing an 0.8 kcal. increment or a total difference of 5.6 kcal. The former conformation, therefore, is the more stable.

The *cis–syn–cis*-perhydrophenanthrene has a 1,3-(p) (p) interaction of the type considered above in the *cis–syn–cis*-perhydroanthracene. If the parameter 4.8 kcal. is invoked for this interaction the total energy difference becomes 7.2 kcal. It is difficult to estimate the energy difference of *trans–syn–trans*-perhydrophenanthrene. In addition to the boat conformation for the central ring,[3] the bonds forming the angle define an eclipsed conformation giving rise to an interaction of the type shown in Fig. 5. The contribution of this interaction is not easily evaluated; however, the total energy difference of the *trans–syn–trans* form should be greater than 5.6 kcal.

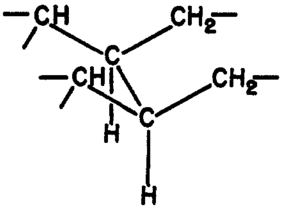


Fig. 5.

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The Chemistry of Aliphatic Phosphonic Acids. I. Alkylation of Methanediphosphonic Acid[1]

BY GENNADY M. KOSOLAPOFF

RECEIVED OCTOBER 30, 1952

Some time ago we reported a study of the alkylation at the central carbon atom of trialkyl phosphonoacetates, *i.e.*, compounds of the general type $(RO)_2P(O)CH_2CO_2R$.[2]

The phosphonoacetates can be regarded as partial phosphorus-bearing analogs of dialkyl malonates. The ready alkylation and dialkylation of the former showed very nicely the active methylene character of the central group in these esters, but the question still remained as to the source of the active methylene character, for this could have originated solely in the carboxylic end of the molecule.

In order to resolve this question we investigated the possibility of alkylation of tetraalkyl methanediphosphonates, *i.e.*, esters of the general type $(RO)_2P(O)CH_2P(O)(OR)_2$, which can be regarded as the true phosphorus analogs of the malonates. A few minor points relative to the preparation of the tetraethyl esters were clarified and it was established that esters higher than tetraethyl cannot be very satisfactory model substances, owing to very high boiling points. Since the purification of the reaction products centers exclusively in the fractionation procedures, the use of very high-boiling materials is undesirable. The sensitivity of the methyl esters to hydrolysis made such esters equally undesirable.

It was found that tetraethyl methanediphosphonate reacts readily with potassium in inert solvent, the reaction being quite exothermic. The resulting potassio derivative alkylates moderately readily with *n*-butyl bromide yielding the corresponding tetraethyl pentane-1,1-diphosphonate, which was characterized and hydrolyzed to the free acid which was also characterized. The rather unsatisfactory yields of the products effectively precluded the extension of the work to dialkylation reactions. However, the monoalkylation was demonstrated beyond doubt. The behavior of the mixture indicated that a considerable portion of the ester undergoing alkylation suffers ester-cleavage with subsequent formation of partial sodium salts. Such reactions have been noted for other esters of phosphonic acids[3] and present a serious problem to be solved in respect to satisfactory isolation of such substances.

The activity of the hydrogen in the methylene group of the diphosphonate can be attributed to

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[1] Presented at the Southeastern Regional Meeting, October, 1952.

[2] G. M. Kosolapoff and J. S. Powell, THIS JOURNAL, **72**, 4198 (1950). See the bibliography in this paper for earlier references.

[3] V. S. Abramov and M. N. Morozova, *Zhur. Obshchei Khim.*, **22**, 257 (1952).