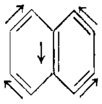
of the individual structures (2) and (3). It is believed this transition corresponds to the weak long axis polarized 3100 Å. transition actually found.[18,21]

It is difficult to make energy predictions involving the E states, because of the resonance among normal structures. The lowest energy E state, based on just the first normal structure,[22] has the vectors phased as



The transition energy before resonance among normal structures as considered would be expected to be not far from the value for an infinitely long polyene. The transition moment vector is directed along the short axis. The three vectors on the left cancel approximately, as they do exactly with the B_{1u} state of benzene, so that the intensity should be of the order of that expected for *s-cis*-butadiene (which in turn is the same as for ethylene, according to the expected trigonometry). This predicted polarization and intensity corresponds quite well to that observed for the second singlet transition for naphthalene at 2700 Å. which is accordingly assigned as N,E.

The observed transition energies to this first E state change over a series of cata-condensed hydrocarbons in a regular fashion.[23] They approach a limit at *ca.* 5500 Å. which is not far from the limiting absorption for polyenes. If we accept the classification scheme given above, it then appears that resonance among normal structures lowers the ground state much more than the first E state in benzene (2000 Å.) and naphthalene (2700 Å.) but as the molecules become bigger the effects become more nearly equal so that in the limit the N,E transition energy is about the same as would be expected if there were no resonance among normal structures.

Comparison with the Orbital Approach.—When a molecule has only a single normal structure the implication is that there is a high degree of localization of electrons in the bonds. Resonance among normal structures, as is well known, is the way the classical theory of valence accommodates itself to delocalization. The molecular orbital approach stands in a complementary position regarding localization effects. Thus with extreme delocalization (as with dyes) the molecular orbital approach is particularly natural, while with considerable localization (as found in the carotenes) the orbital theory also needs to accommodate, which it does through configurational interaction. Just as we "understand" resonance among valence bond structures by adopting an orbital point of view, so we can hope to understand many of the effects of configurational interaction by qualitative interpretations using structures.

SEATTLE, WASHINGTON

(21) M. Kasha and R. V. Nauman, *J. Chem. Phys.*, **17**, 516 (1949); D. S. McClure and O. Schnepp, *ibid.*, **23**, 1575 (1955); D. S. McClure, *ibid.*, **24**, 1 (1956).

(22) The sum of vectors is the same for the other normal structures.

(23) H. B. Klevens and J. R. Platt, *J. Chem. Phys.*, **17**, 470 (1949).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, STATE UNIVERSITY OF NEW YORK, COLLEGE OF FORESTRY]

Reactivities of Twisted or Stretched C=C Double Bonds[1]

BY M. SZWARC AND F. LEAVITT

RECEIVED FEBRUARY 13, 1956

The reactivities of aromatic and olefinic compounds toward methyl radicals, measured by their methyl affinities, are related to the corresponding localization energies. This relation is demonstrated for a series of aromatic hydrocarbons. It is pointed out that localization energies are proportional to β, the exchange integral. Bending of an aromatic hydrocarbon out of planar configuration or twisting or stretching a C=C double bond decreases the overlap of p orbitals and, hence, decreases β. Consequently, the localization energies of such molecules decrease, and the reactivities and the methyl affinities of the respective compounds increase. These conclusions are tested on a series of suitable compounds and their validities are fully demonstrated.

The reaction $CH_3 + A \rightarrow A{\cdot}CH_3$, where A represents an aromatic or an olefinic molecule, is well suited for studies of relations between the reactivity and the chemical constitution of molecules. The values of the relative rate constants of such bimolecular reactions, further referred to as methyl affinities, can be determined easily by a special experimental technique devised for this purpose and already described in earlier communications.[2,3] The results, obtained from studies of several classes of compounds,[2-6] indicate that simple relations exist between methyl affinities and other structural properties of the respective molecules. One such a relation recently has been discussed by Coulson[7] who has shown that logs of methyl affinities of aromatic hydrocarbons are related linearly to the corresponding localization energies. This relation illustrated by Fig. 1, has been extended now, and its validity has been demonstrated for a few more hydrocarbons not considered in Coulson's paper (see also Table I).

Localization energies are calculated by solving the appropriate secular equations, and the results appear in the form $C_i{\cdot}\beta$, where C_i's are numerical coefficients determined entirely by the form of the secular equations, while β is the so-called exchange integral. We notice, therefore, that the localization energies decrease whenever the coefficients C_i's or the exchange integral β decrease in their

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[1] This paper reports the continuation of studies communicated previously to THIS JOURNAL (M. Levy, M. S. Newman and M. Szwarc, THIS JOURNAL, **77**, 4225 (1955). The latter investigation was supported by a grant from the National Science Foundation.

(2) M. Szwarc, *J. Polymer Sci.*, **16**, 367 (1955).

(3) M. Levy and M. Szwarc, THIS JOURNAL, **77**, 1949 (1955).

(4) A. Rembaum and M. Szwarc, *ibid.*, **77**, 4468 (1955).

(5) F. Leavitt, M. Levy, M. Szwarc and V. Stannett, *ibid.*, **77**, 5493 (1955).

(6) M. Levy, M. S. Newman and M. Szwarc, *ibid.*, **77**, 4225 (1955).

(7) C. A. Coulson, *J. Chem. Soc.*, 1435 (1953).

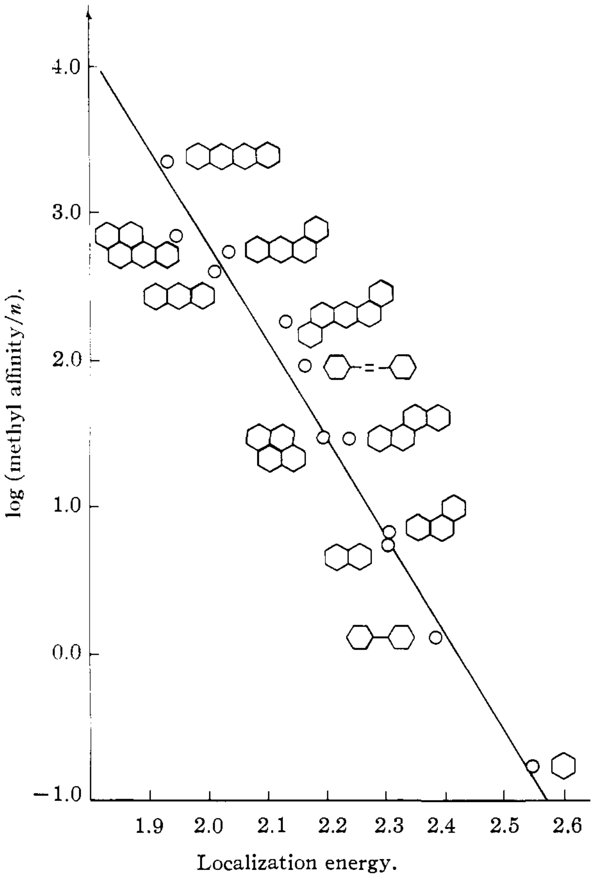

Fig. 1.

TABLE I

Hydrocarbon	Methyl affinities[a]	n	Localization energies,[b] β^{-1}
Benzene	1	6	2.54
Biphenyl	5	4	2.38
Naphthalene	22	4	2.30
Phenanthrene	27	4	2.30
Chrysene	57	2	2.24
Pyrene	125	4	2.19
trans-Stilbene	183	2	2.16
Dibenzanthracene*	370	2	2.13
Benzanthracene*	515	1	2.04
Anthracene	820	2	2.01
Benzpyrene*	670	1	1.94
Naphthacene	9250	4	1.93

[a] The values of methyl affinities are taken from reference 3. Methyl affinities of the starred compounds were determined in the course of the present investigation. [b] The localization energies are given in a paper by E. C. Kooyman and E. Farenhorst, *Trans. Faraday Soc.*, **49**, 58 (1953), see also C. A. Coulson, reference 7.

values. Such a decrease leads in turn to an increase in the reactivity, and hence in the methyl affinity of the respective compounds.

The exchange integral β depends on the overlap of two adjacent p orbitals, and its value is lower for a smaller overlap. In planar aromatic hydrocarbons and in normal C=C double bonds, the p orbitals are mutually parallel and they overlap considerably. However, if an aromatic hydrocarbon is bent out of plane or if a C=C double bond is twisted, the respective p orbitals rotate in such a manner that their overlap decreases. This point is illustrated schematically by Fig. 2. Hence, the bending of an aromatic molecule or the twisting of a C=C double bond decreases the exchange integral β and, consequently, it should increase the reactivity and the methyl affinity of the respective compound.

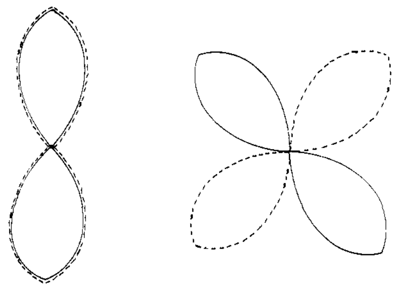

Fig. 2.

The length of a carbon to carbon bond in aromatic molecules is essentially a constant; hence, the exchange integral β also is a constant. However, if the length of a C=C bond is increased, *i.e.*, if such a bond is stretched, then the overlap of p orbitals and, therefore, the exchange integral β would decrease. Consequently, the reactivity and the methyl affinity of aromatic hydrocarbons, molecules of which involve stretched C=C double bonds, should be abnormally high.

All these effects discussed above have been demonstrated on a series of properly chosen compounds, and the results are described and discussed in the present paper.

The Non-planar Aromatic Hydrocarbons.—The determination of methyl affinities of some non-planar aromatic hydrocarbons was reported in previous communication.[6] The compounds studied belong to the class of benzo[C]phenanthrene derivatives, and it was shown by Newman and his co-workers[8] that the steric hindrance interferes with the planar configuration of these molecules. The steric hindrance, and therefore the extent of bending the molecule out of planar configuration, increases with the bulkiness of the substituents introduced into 1- or 12-position of benzo[C]phenanthrene and, of course, 1,12-disubstituted molecules are more strongly bent than the corresponding monosubstituted ones. From our previous discussion we predict, therefore, that the increasing extent of bending of the molecule should be accompanied by a rise in the methyl affinity of the respective hydrocarbon, and the results, shown in Table II, confirm fully these conclusions.

Molecules Involving Twisted C=C Double Bonds.—Inspection of the model of the bis-diphenylene ethylene molecule shows that the enormous steric strain, resulting from the close proximity of the hydrogen atoms on the 1,8,1′ and 8′ carbon atoms, prevents the co-planar configuration of this molecule. To release this strain the two planar fluorene wings of this molecule have to be turned round the central C=C bond (such a

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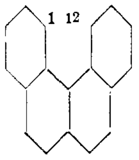
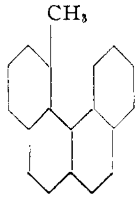
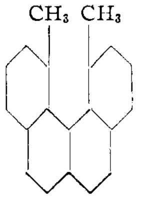
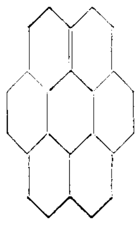
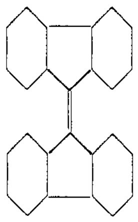
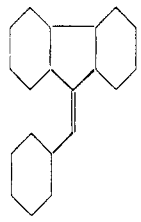
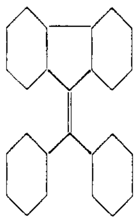
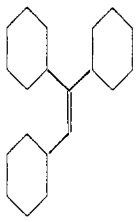
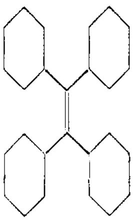
(8) M. S. Newman and W. B. Wheatley, THIS JOURNAL, **70**, 1913 (1948); M. S. Newman, *ibid.*, **62**, 2295 (1940).

TABLE II

				
Methyl affinity at 85°	55–75[a]	108[a]	183[a]	285
	Benzo [C] phenanthrene and all the mono-methyl derivatives containing the methyl group in positions other than 1 or 12.			Hexahelicene[b]

[a] These data are taken from ref. 6. [b] The synthesis of this hydrocarbon is to be reported by M. S. Newman and D. Lednicer.

TABLE III

					
	A	B	C		
Methyl affinity at 85°	1370	820	~15	85	<25

suggestion was forwarded by Bergmann[9]). This rotation leads, of course, to a twist in the respective π electron system (see Fig. 2), and in view of what has been said before, it should increase the reactivity of the respective compound. To test this prediction, methyl affinity of bis-diphenylene ethylene and of other related compounds has been determined. The results are collected in Table III, inspection of which leads to the following conclusions.

The presence of bulky groups attached to a C=C double bond decreases its reactivity.[4,5] This effect is due to the shielding action of such groups, and consequently, the approach of methyl radicals to the reactive center[11] is hindered. To illustrate this point let us compare the methyl affinity of triphenylethylene with that of tetraphenylethylene. The C=C double bond in the latter molecule is completely shielded, and consequently the methyl affinity of tetraphenylethylene is very low, namely, less than 25. On the other hand, the shielding by the three phenyl groups in triphenylethylene is not as complete as in the former compound, and thus the methyl affinity of this molecule is considerably higher, namely, 85. A similar relation might be expected in the pair of molecules, phenyldiphenylene-ethylene (compound B in Table III) and bis-diphenylene-ethylene (compound A in Table III). However, here the tetra-substituted compound (A) shows a *higher* methyl affinity than the ter-substituted one (B). This result indicates that there is some additional factor which is responsible for the high reactivity of the C=C bond in bis-diphenylethylene and, moreover, that this additional factor is not operative in compound B. Since the C=C bond in the former compound is twisted, while no twisting takes place in compound B, it seems that it is the twisting of the C=C double bond which is responsible for the increase in the reactivity.

Much more convincing evidence is provided by comparing the methyl affinities of bis-diphenylene-ethylene (A) and of diphenylene-diphenylethylene (C). Superficially it appears that these two compounds should behave similarly—the shielding of the C=C bond seems to be the same. However, a close inspection shows that the free rotation around the C—Ph bonds in compound C removes the steric strain which would occur in the planar configuration of the molecule and, thus, the twisting of the central C=C bond needs not to take place at all. Hence, the methyl affinity of compound C should be similar to that of tetraphenylethylene, and indeed it is. On the other hand, the methyl affinity of the twisted bis-diphenylene-ethylene should be much higher, and indeed it is enormously greater than that of compound C (1400 as compared with 15).

The increase in the reactivity of a twisted double bond should not be interpreted as a result of formation of a diradical. The spin of the twisted molecule still remains zero. The twisting is a different process from the excitation from singlet to triplet state, although the twisting process lowers the singlet–triplet excitation energy.

Finally, let us remark that the increase in the reactivity of a compound B, as compared with

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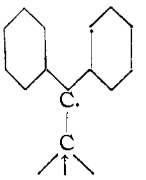
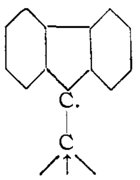
(9) E. D. Bergmann, *et al.*, *Bull. soc. chim., France*, **463**, 217 (1948) (see also reference 10).

(10) J. M. Robertson, "Organic Crystals and Molecules," Cornell Univ. Press, Ithaca, N. Y., 1950, p. 214.

(11) In order to compare properly the reactivities of various centers and groups, it is desirable to point out that the methyl affinity of an isolated phenyl group (*i.e.*, of benzene) is only 1, of biphenyl 5, while that of ethylene is about 75 and of styrene 1630.

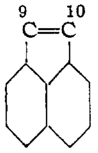
triphenylethylene, is essentially due to the greater resonance energy of the fluorenyl radical as compared with the diphenylmethyl radical. These



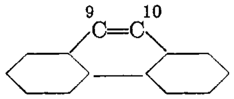


radicals are formed by attack of methyl radicals on the lower C carbons of these molecules. Furthermore, the interaction of two phenyl groups in *cis* configuration lowers reactivity of triphenylethylene since this interaction interferes somehow with the planarity of the diphenylmethyl radical (see reference 5 for further discussion of this point). On the other hand, the more rigid structure of the fluorenyl radical resists such an interference and consequently the methyl affinity of compound B approaches the value observed in the case of diphenylethylene.

Molecules Involving Stretched Double Bonds.—Inspection of the structure of acenaphthalene reveals that the 9–10 C═C bond of this molecule is considerably stretched



We have determined now the methyl affinity of this compound to be 1030, and this value seems to be much higher than would be expected for a hydrocarbon of this complexity with normal 1.39 C═C



bonds. This point is better appreciated if one compares the methyl affinity of acenaphthylene with that of phenanthrene. The 9–10 bond of this compound is probably comparable to the 9–10 bond of acenaphthylene; however, in contradistinction to the latter, its length is normal. The methyl affinity of phenanthrene is only 27, *i.e.*, much lower than that of acenaphthylene.

Experimental

All the experiments reported in this paper were carried out in toluene solution at 85°. The apparatus and the experimental technique applied in these studies are described fully elsewhere.[2,3]

Hexahelicene was prepared by Professor Melvin S. Newman and D. Lednicer of Ohio State University. Bis-diphenylene-ethylene and phenyldiphenylene-ethylene were kindly supplied to us by Professor E. D. Bergmann (Tel-Aviv). The latter two compounds had sharp melting points, namely, 187 and 76°, respectively. The corresponding literature values are 187–188°[12] and 76°.[13]

TABLE IV
Toluene Solution, 85°

Compound	Mole %	CH_4/CO_2	k_2/k_1	Methyl affinity[a]
Phenyldiphenylene-ethylene	0.5	0.368	160	
	1.0	.262	150	
	1.5	.206	150	820[b]
	2.5	.158	125	
	4.5	.107	110	
Diphenyldiphenylene-ethylene	0.125	0.664	1	
	.25	.660	3	Av.
	.50	.658	2	~15
	.84	.660	1	
Bis-diphenylene-ethylene	0.50	0.351	180	
	1.20	.202	190	Av.
	2.0	.140	180	1370
	3.6	.114	130 (?)	
	.33	.411	187[c]	
Hexahelicene	0.524	.552	38	285
Benzopyrene	0.08	0.620	85	
	.16	.580	91.5	667
	.32	.523	90.5	
Benzanthracene	1.0	0.395	68.5	514
Dibenzanthracene	0.28	0.580	51.5	
	.39	.561	49	370
	.41	.554	47	
Acenaphthylene	0.5	0.380	150	
	1.0	.279	137	
	1.5	.201	154	1030
	3.0	.138	127	
	4.5	.108	115	

[a] Methyl affinity = $7.5\times(k_2/k_1)$; CH_4/CO_2 in pure toluene = 0.665. [b] In view of the trend observed in the k_2/k_1, it seems that the lowest value obtained at the highest concentration of the compound is the most reliable. [c] This experiment was carried out with a recrystallized sample of bis-diphenylene-ethylene.

Diphenylene-diphenylethylene was prepared in our laboratories by Dr. Glennie by condensing lithium fluorenyl with benzophenone and dehydrating the resulting alcohol. After a few crystallizations, the colorless needles of the compound melted sharply at 227–228°, the literature value[14] being 225°.

Benzpyrene, benzanthracene, dibenzanthracene and acenaphthylene were acquired commercially. After recrystallization their purity was checked by the sharpness of the melting points. All the experimental data are collected in Table IV.

Acknowledgment.—We wish to thank both Dr. Bergmann and Professor Newman for their kindness in supplying us with the required compounds. We are indebted to Professor Coulson for an interesting and stimulating discussion and to the National Science Foundation for their most generous financial support of these studies.

SYRACUSE, NEW YORK

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(12) C. Graebe and V. Mantz, *Ann.*, **A290**, 241 (1896).

(13) J. Thiele, *Ber.*, **33**, 852 (1906); J. Thiele and F. Henle, *Ann.*, **A347**, 296 (1906).

(14) W. Schlenk and E. D. Bergmann, *ibid.*, **A463**, 217 (1928).