[Contribution from the Department of Chemistry of the University of Oregon]

CHEMICAL REACTIVITIES OF ARYLCYCLOALKENES. III. MOLECULAR COMPOUNDS OF TRINITROFLUORENONE WITH SOME SUBSTITUTED NAPHTHALENES[1, 2]

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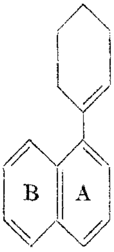
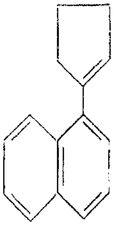
In previous papers in this series (1, 2) we reported investigations on the reactivities of the four olefins, 1-(1′-naphthyl)-1-cyclohexene (I), 1-(1′-naphthyl)-1-cyclopentene (II), 1-(2′-naphthyl)-1-cyclopentene (III), and 1-(2′-naphthyl)-1-cyclohexene (IV), toward catalytic hydrogenation *via* Adams' platinum (order II = III = IV > I), Diels-Alder condensation with maleic anhydride (order II ≅ III > IV > > I), and polarographic reduction (II = III > IV > I). These orders of reactivity were explained in terms of two factors, namely (a) steric hindrance to coplanarity, of significance only in the case of I in catalytic hydrogenation and the Diels-Alder reaction, and (b) conjugation of the cycloalkenyl double bond with the naphthalene nucleus, of significance only in electroreduction and the Diels-Alder reaction and greater in magnitude for the cyclopentenyl ring than for the cyclohexenyl ring. The present paper reports an extension of this program to studies of the stabilities of the 2,4,7-trinitrofluorenone (TNF) molecular compounds (also known as "complexes") with I–IV, 2-methylnaphthalene (V), and 1-methylnaphthalene (VI).



I



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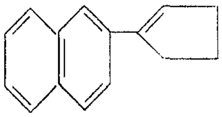

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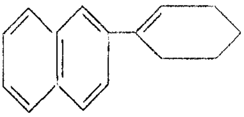

IV

In all cases molecular ratios of hydrocarbon to TNF in the complex were found to be 1:1 in glacial acetic acid solution at room temperature (conditions identical with those used subsequently for studies on the apparent stability constants of these complexes) by a spectrophotometric method of continuous variations. In addition solid crystalline complexes (also 1:1) were obtained for II–VI, though I failed to produce any isolable complex under the same conditions. A melting-point composition curve indicated the formation of a complex, of molar ratio not less than 2:1 (TNF:I), having an incongruent melting point (3b). A similar

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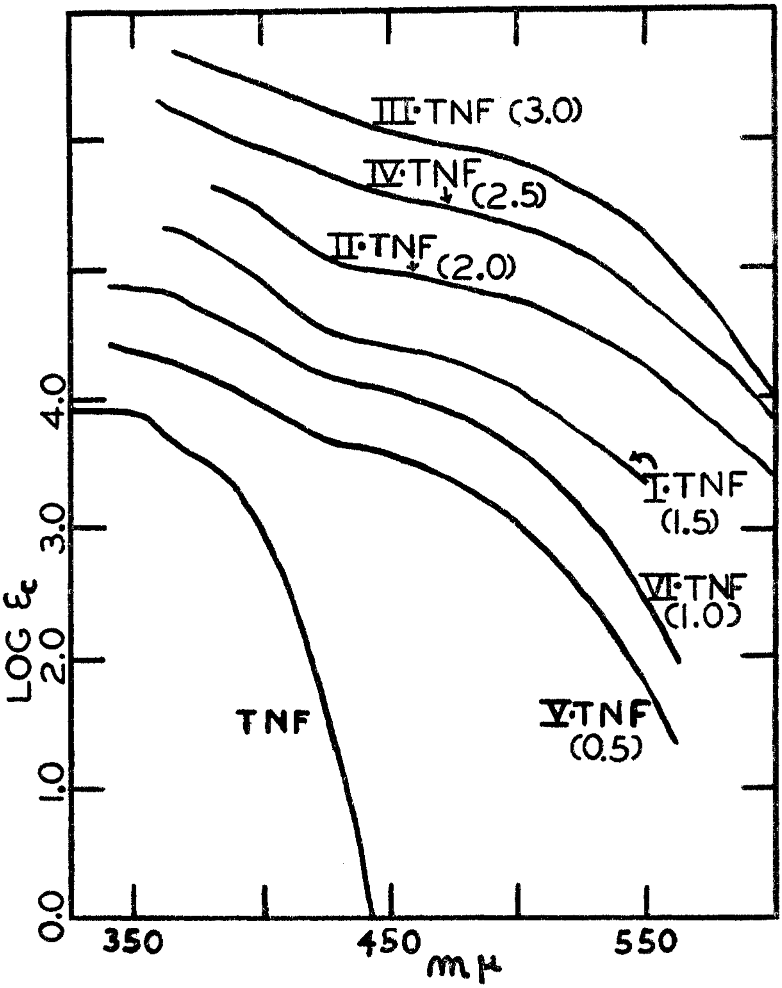

FIG. 1. ABSORPTION SPECTRA FOR TNF AND SIX OF ITS 1:1 MOLECULAR COMPOUNDS. Solvent glacial acetic acid. Numbers in parentheses represent upward vertical displacements of the respective curves.

peculiarity for I is not found in the case of the picrates of I–IV, all of which occur as crystalline 1:1 complexes with I-picrate having the highest melting point (1). Indeed it was precisely the non-conformance between our postulations on hindrance to coplanarity in I and the theory of Orchin relating coplanarity of the hydrocarbon moiety to the melting point of its picrate (4) which led us to investigate TNF-complex formation. An interpretation of this discrepancy will be reserved for a subsequent paper.

Spectrophotometric studies of the apparent stability constants of the 1:1 complexes were made at a wavelength of 460 mμ where absorbances of acetic acid solutions of either I–VI or TNF alone were exceedingly small and the absorption curves for the complexes exhibited broad shoulders (Fig. 1). Results are

TABLE I

EXTINCTION COEFFICIENTS AND APPARENT STABILITY CONSTANTS FOR 1:1 MOLECULAR COMPOUNDS OF SIX SUBSTITUTED NAPHTHALENES WITH 2,4,7-TRINITROFLUORENONE[a]

Hydrocarbon	C_{HO}[b] moles/l.	C_{TO}[c] × 10^3 moles/l.	K (stability)	ϵ_C[d] at 460 mμ
I	0.02–1.02	0.5–16.0	16.0 ± 0.9	748
II	0.03–1.06	0.2–7.9	21.6 ± 0.5	922
III	0.01–0.28	1.0–7.0	64 ± 2	1010
IV	0.02–0.53	0.3–4.2	50.5 ± 1.5	1060
V	0.02–1.42	1.3–9.9	27.6 ± 0.6	988
VI	0.02–6.27	0.2–5.0	27.5 ± 0.7	1000

[a] Solvent: glacial acetic acid. [b] Total concentration of hydrocarbon (free and complexed) in solution. [c] Total concentration of TNF (free and complexed) in solution. [d] Molar extinction coefficient of complex.

summarized in Table I, examination of which shows that the two methylnaphthalenes V and VI exhibit identical stabilities in their TNF complexes. Such is not the case for the cycloalkenylnaphthalenes where the 2-isomers give more stable complexes than do the corresponding 1-isomers. If one considers the stability of the complex as a measure of the reactivity of the cycloalkenylnaphthalene toward TNF then one has III > IV > II > I in order of reactivity. This order is not only different from all of those found in previous studies but is, at least within the accuracy of measurement, quantitatively ideal inasmuch as the data fit the relationship $K_{III}:K_{IV}::K_{II}:K_I$ (where the subscripts refer to the respective hydrocarbons), expected *à priori* only in the event that the reactivity of each one of the compounds I–IV is determined by (a) the nature of the substituent on the naphthalene nucleus and (b) the position of substitution on the naphthalene nucleus. Such a relationship could scarcely be expected to hold if an exceptional steric hindrance to coplanarity of the type postulated for I in catalytic hydrogenation and Diels-Alder condensation were significant here. Nonetheless, the fact that K is smaller for I and II than for V and VI (while K is largest for III and IV) indicates that some additional factor prevails in the case of the 1-cycloalkenylnaphthalenes.

Although the steric configuration of the TNF molecule is unknown it seems reasonable to assume that the carbon skeleton may attain planarity in solution, such as has been proposed for the fluorene molecule (5, 6), and would probably be planar in its molecular compounds. Combining such proposed planarity with approximate bond lengths and angles for the molecules (5, 7) and with the concepts of molecular compounds such as postulated by Mulliken (8) and Landauer and McConnell (9), we found it possible to construct models (Figs. 2 and 3) of the TNF complexes which are, we believe, at least qualitatively consistent with the relative stabilities found. These models were constructed as follows: (a) To take account of the fact that olefins of themselves do not form isolable polynitroaromatic complexes, while naphthalene and alkylnaphthalenes do, we first superimposed, as a sort of anchor point, one benzenoid ring of TNF directly over the B-ring of I–IV. (b) To preserve some semblance of symmetry but still allow

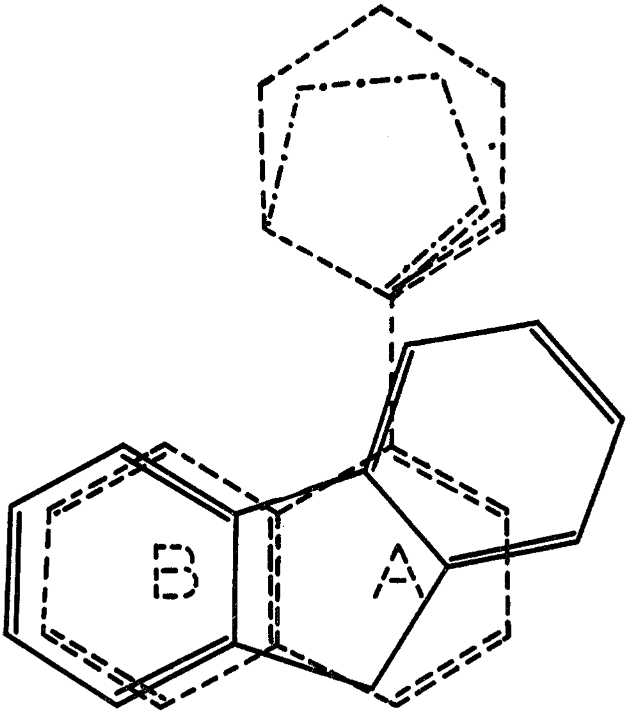

FIG. 2. PRESUMED GEOMETRY FOR 1:1 COMPLEX OF TNF WITH I OR II. Solid lines represent carbon skeleton of TNF. Broken lines represent the 1-cycloalkenylnaphthalene.

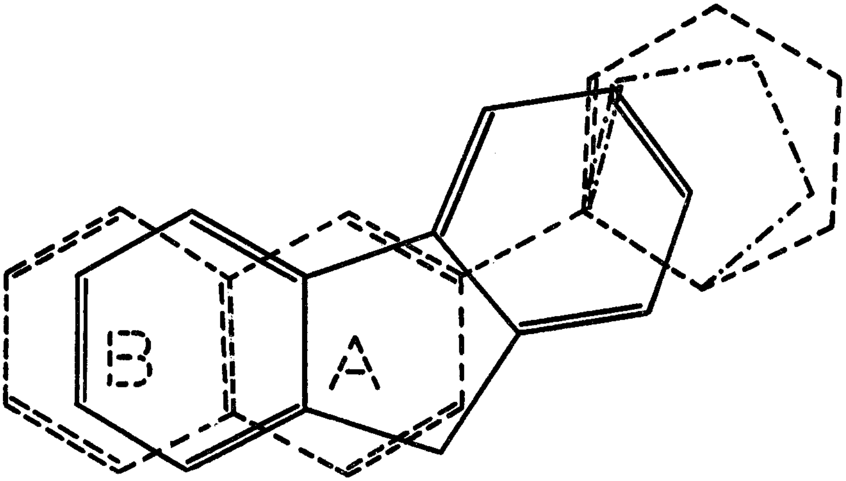

FIG. 3. PRESUMED GEOMETRY FOR 1:1 COMPLEX OF TNF WITH III OR IV. Solid lines represent carbon skeleton of TNF. Broken lines represent the 2-cycloalkenylnaphthalene.

maximum acid-base interaction through the π-electrons we have then translated the TNF molecule right or left (9) along the horizontal symmetry axis of the naphthalene ring so as to enhance coverage of the pivotal bonds (joining the naphthyl and cycloalkenyl moieties), where partial double bond character exists, and the cycloalkenyl double bonds, by the other benzenoid ring of the TNF molecule. Though orientations in these models are, therefore, highly arbitrary they serve to point out the fact that the geometry of the TNF molecule is such as to allow better overlap of the whole unsaturation system in a 2-cycloalkenylnaphthalene than in the corresponding 1-cycloalkenylnaphthalene.

In summary, we believe that our results thus far bearing on the problem of coplanarity *versus* reactivity for olefins I–IV are best interpreted as follows: (a) Olefins III and IV may be considered completely coplanar in TNF complex-formation in solution, catalytic hydrogenation, condensation with maleic anhydride, polarographic reduction, and absorption of ultraviolet light.[2a] (b) Olefin I may be considered non-coplanar in all of these cases. (c) Olefin II, seems less definite in its geometric configuration. Thus in TNF complex-formation and in absorption of ultraviolet light, cases where *bona fide* chemical reaction is not involved, we feel it is preferentially non-coplanar (as is consistent with the geometric construction of the molecule), while in other cases, where *bona fide* chemical reaction is involved, we detected no evident lack of coplanarity or hindrance thereto. Work is now underway in an effort to ascertain if this apparent inconsistency in the configuration of II may be the result of a very low energy barrier to the formation of a coplanar transitional complex during chemical transformation.

EXPERIMENTAL[3]

Starting materials. The *olefins* I–IV were obtained by dissociation of the corresponding picrates, as prepared and described by Klemm and Hodes (1). *2-Methylnaphthalene,* Eastman Kodak white label, was distilled and then crystallized from ethanol, m.p. 35.3–36.0°. *1-Methylnaphthalene,* Reilly Tar and Chemical Corporation 98%, was distilled twice, b.p. 92–93°/4.6 mm. *TNF,* prepared according to *Organic Syntheses* (10) was recrystallized from methyl ethyl ketone-95% ethanol (1:1) to constant m.p., 175–176°. *Glacial acetic acid* was ACS grade 99.5%.

Stoichiometry of the TNF molecular compounds. To prepare crystalline compounds, solutions of (a) 1 g. of the hydrocarbon in 5 ml. of hot glacial acetic acid and (b) an equimolar quantity of TNF in 15 ml. of the same solvent were mixed. The orange-red needles which separated on cooling were recrystallized from acetic acid to constant m.p.: *II•TNF,* 124–125°; *III•TNF,* 147.5–148.5°; *IV•TNF,* 128–129°; *V•TNF,* 125–126°;[4] *VI•TNF,* 161–162°.

[2a] A paper reporting the results of spectral studies on I–IV and analogous olefins is in preparation. Some possible discrepancy in the case of IV will be discussed there.

[3] Melting points are uncorrected. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Illinois.

[4] Orchin, Reggel, and Woolfolk (15), on the basis of a presumedly erroneous nitrogen analysis, reported the formation of the complex V•2-TNF under the same conditions. Since the physical properties of our 1:1 complex agreed remarkably well with those reported by these workers, we subjected mixtures of V and TNF to a complete phase study, which showed definite evidence for the formation of a stable 1:1 complex but no indication of the formation of any other complex.

Anal. Calc'd for $C_{15}H_{14} \cdot C_{13}H_5N_3O_7$: C, 66.01; H, 3.76; N, 8.25.
Found II•TNF: C, 65.97; H, 3.76; N, 8.02.
Found III•TNF: C, 65.78; H, 3.90; N, 8.10.
Calc'd for $C_{16}H_{16} \cdot C_{13}H_5N_3O_7$: C, 66.53; H, 4.04; N, 8.03.
Found IV•TNF: C, 66.46; H, 4.09; N, 8.11.
Calc'd for $C_{11}H_{10} \cdot C_{13}H_5N_3O_7$: C, 63.02; H, 3.31; N, 9.19.
Found V•TNF:[4] C, 62.96; H, 3.34; N, 9.32.
Found VI•TNF: C, 62.92; H, 3.35; N, 9.53.

I gave no isolable complex even from more concentrated solutions, or from chloroform or ethyl acetate alone or mixed with acetic acid. A mixture of I with double the molar quantity of TNF deposited only TNF from acetic acid solution.

Phase studies (m.p. *versus* composition) on mixtures of I or V[4] and TNF were made by the thaw-melt method (3a).

Spectral studies were made with a Beckman DU Spectrophotometer using a tungsten filament as source and Corex cuvettes. Samples for use in the spectrophotometric method of continuous variations (11) were prepared by mixing varying measured volumes, x ml., of 0.02–0.05 M solutions of hydrocarbon in glacial acetic acid with $(10 - x)$ ml. of an equimolar solution of TNF in the same solvent. Absorbance was read at 460 mμ.

Equilibrium constant measurements. The method was a modification of the procedures of Benesi and Hildebrand (12) and Takemura, Cameron, and Newman (13). Standard solutions containing varying concentrations of TNF in glacial acetic acid were prepared. A measured volume (at least 2 ml.) of one of these solutions was added to a weighed amount of hydrocarbon contained in a tared 10-ml. volumetric flask. Other flasks containing varying weights of the same hydrocarbon were prepared likewise. The contents of each flask were diluted with solvent (glacial acetic acid) to about 8 ml., air in the flask was flushed out with nitrogen, and heat was applied, if necessary, to bring solids into solution. The stoppered flask was allowed to stand in a cabinet at about 25° for 1–2 hours. Solvent was added to volume, the gross weight was measured, and the total absorbance at 460 mμ was immediately ascertained (using pure solvent in the reference cell). A blank containing only the hydrocarbon in glacial acetic acid was run at the same time. The absorbance of the complex, Ac, was obtained by correcting the total absorbance for the presence of uncomplexed hydrocarbon and uncomplexed TNF (See Fig. 1). The range of concentrations used for each hydrocarbon is given in Table I. The upper limit of concentration was dictated by solubility considerations. Certain of these same solutions were used to obtain absorption curves for the complexes over the range 330–600 mμ (Fig. 1).

HANDLING OF DATA

Following Benesi and Hildebrand (12) one can express the apparent stability constant, K, for complex formation by the equation

$$K = \frac{C_C}{N_H(C_{TO} - C_C)},$$

where C_C is the molar concentration of the complex, C_{TO} is the total (free plus complexed) molar concentration of TNF, and N_H is the mole fraction of uncomplexed hydrocarbon—present in relatively large amounts—all at equilibrium. After making the substitution $C_C = A_C/\epsilon_C$, where ϵ_C is the corresponding molar extinction coefficient, one gets

$$\frac{A_C}{N_H C_{TO}} = K\epsilon_C - K\left(\frac{A_C}{C_{TO}}\right), \qquad \text{(Equation 1)}$$

of the linear form $x = a + bz$.

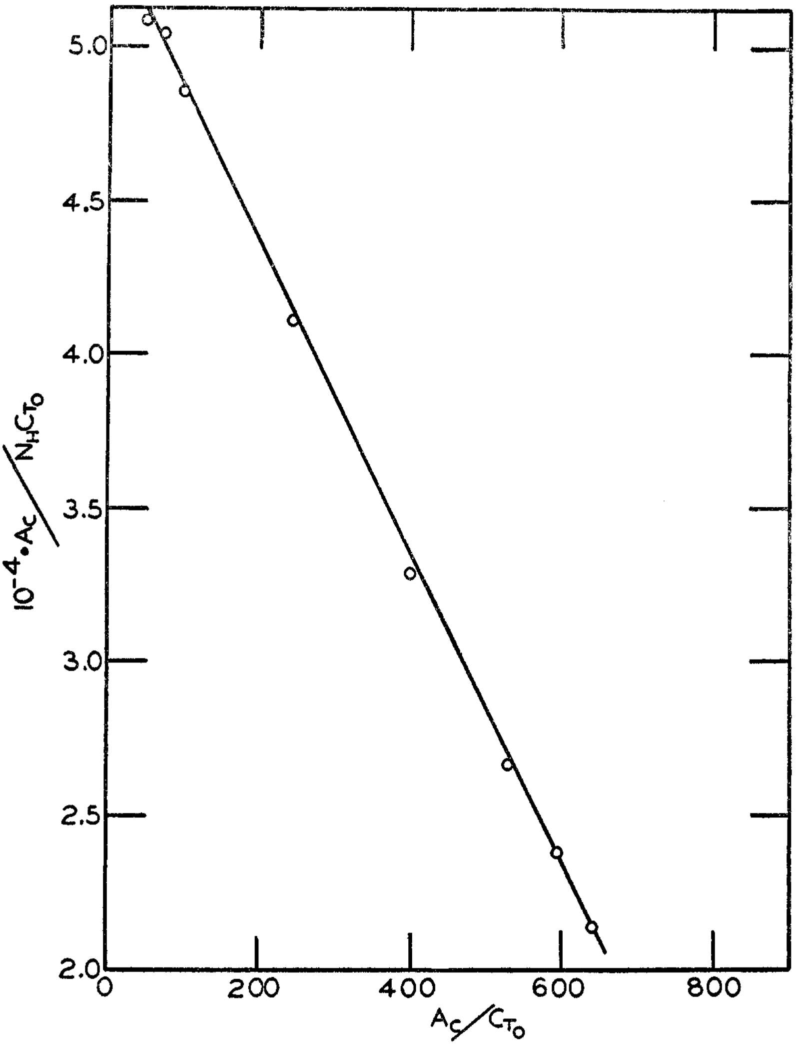

Fig. 4. Plot of Equilibrium Data for the Reaction IV + TNF $\rightleftharpoons$ IV•TNF According to Equation 1.

Preliminary experiments were conducted using molar concentrations of hydrocarbon much larger than C_{T_0} so that $N_H \cong N_{H_0}$, where N_{H_0} is the readily calculable mole fraction of total hydrocarbon (free and complexed). The linear least squares plot of the calculated approximate x (designated as x') *versus* z allowed determinations of approximate values for a and b and, thence, for ϵ_C (designated as ϵ_C'). Extension of measurements to the region where $N_H \not\cong N_{H_0}$ and adjustment of the previous data was then made by use of the equation

$$x = x'\left(\frac{n_{HO}}{n_{HO} - \frac{A_C}{\epsilon_C'}V}\right),$$

where n_{H_0} is the total number of moles of hydrocarbon used in the sample of volume V liters. On the basis of the assumption that the observed data conform to a simple linear normal regression, a 95% fiducial probability level was selected for K (14). Measurements were then extended over a sufficient range of values such that a precision of ±3–6% in K was attainable. A typical plot of the data is shown in Fig. 4 and final data for K and ϵ_C are given in Table I.

SUMMARY

1. 1- and 2-methyl-, cyclopentenyl-, and cyclohexenyl-naphthalenes have been shown to form 1:1 molecular compounds with 2,4,7-trinitrofluorenone in glacial acetic acid at room temperature.

2. Apparent stability constants for these complexes, determined *via* spectrophotometry, showed the effects of substituents 1-methyl = 2-methyl, cyclopentenyl > cyclohexenyl, and 2-cycloalkenyl > 1-cycloalkenyl in fostering stability.

3. Comparison of these results with previous data on the same cycloalkenylnaphthalenes is presented.

EUGENE, OREGON

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