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(Contribution from the H. Fletcher Brown Laboratories
of the University of Delaware)

Isomerism in the Diels-Alder Reaction. II.

The Bromination of Diels-Alder Adducts[1]

by Harold Kwart and Lloyd Kaplan

Abstract

The steric course of bromination of the Diels-Alder adducts of cyclopentadiene and maleic anhydr'.. has been examined. The previously reported structures of two of the three known debromides in this series are found to be inconsistent with the measured dipole moments. Structural assignments are revised to bring all three structures into line with the dipole moment data and with modern concept on the steric course of addition and rearrangement reactions in related bicyclic systems.

(1) The research work being reported here has been supported by the Office of Naval Research under contract N-onr-567(00). c.f. previous paper in this series--This Journal, 74, 3094 (1952).

Craig[2] has examined the reaction mechanism of the ther-

(2) D. Craig, This Journal, 73, 4889 (1951).

mally induced transformation of the endo into the exo adduct of cyclopentadiene and maleic anhydride. Among many other considerations taken into account in his examination, he discusses the nature of the products obtainable on bromination of the residual double bond. Earlier, Alder and Stein[3] had brominated the endo

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(3) K. Alder and G. Stein, Ann., 504, 247 (1933).

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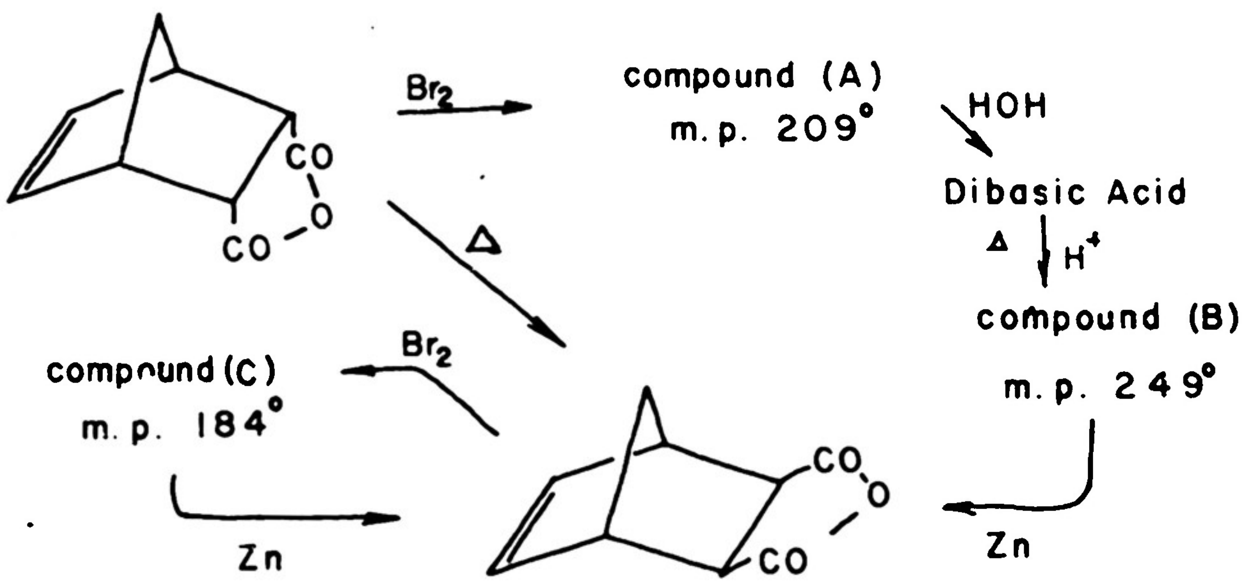
adduct and assigned to the resulting compound A the structure I on the basis of an assumed course of direct trans addition of the elements of bromine to the double bond. Alder and Stein also prepared an isomeric dibromide by careful hydrolysis of A to a dibromo-acid and thermal rearrangement and dehydration of the latter to an anhydride product B. The structure of B was given as II, the 4,5-cis-exo dibromide of the exo-3,6-methylene-1,2,3,4-tetrahydro-cis-phthalic anhydride, i.e., the exo cyclopentadiede-maleic anhydride adduct obtained on treatment of B with zinc in acetic acid. Craig prepared the third known dibromide C by bromination of the exo adduct. He assigned to it the structure of III assuming the bromination had followed a course of direct trans addition and suggested that reformation of exo adduct on debromination of C with zinc establishes the assigned structure.

Chart I contains a summary of these observations.

CHART I



Br2
compound (A)
m.p. 209°
HOH
Dibasic Acid
Δ
H+
compound (B)
m.p. 249°
Zn
Δ
Br2
compound (C)
m.p. 184°
Zn
CO
O
CO

In the course of our work with this system it appeared that the structures of A, B, and C previously assigned may be in error for two reasons; the experimental evidence did not seem to be complete or conclusive in some instances and the assumed reaction course for bromination of the double bond ignored the possibilities of rearrangement previously identified in other double bond addition reactions of this system.[4]

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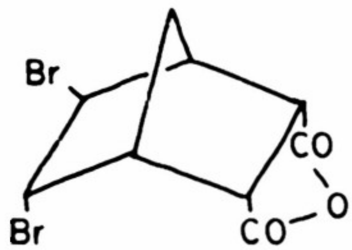
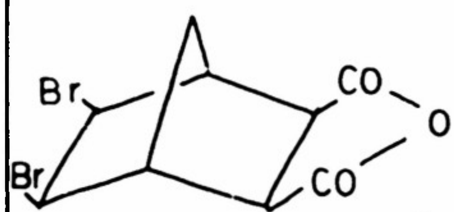
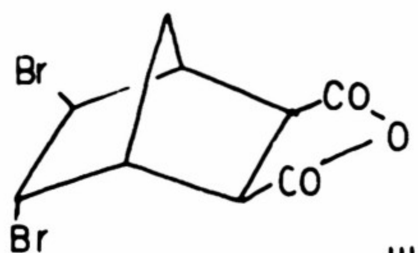
(4) P. D. Bartlett and A. Schneider, This Journal, 68, 6 (1946).
R. B. Woodward and H. Baer, Ibid., 70, 1161 (1948).

It seemed apparent also that a quick test of the validity of the assigned structure was obtainable through a comparison of the computed dipole moments of I, II, and III with the experimental values we have determined and are reporting here for compounds A, B, and C. Table I affords this comparison.

It is to be noted that a large discrepancy exists between the calculated and observed values in the cases of compounds A and B whereas good agreement is demonstrated for compound C. On this basis it is clear that the structure of compound C has been properly assigned, but the structures previously assigned for A and B are seriously in error.

What structures do accord with the observed dipole moments and how could these structures arise in the procedure used for their

TABLE I

Compound	Previously* assigned structure	μ_D calculated	μ_D observed
A	 I	(6.0)** 6.1***	4.5
B	 II	4.4**	3.2
C	 III	(2.9)** 2.5***	2.3

* c.f. reference (2)

** A value of 2.0D[5] for a normal C-Br bond moment is used in this calculation. A value of 4.8D is used for a normal bond moment for the anhydride obtained as a mean experimental value--c.f. experimental section.

*** Value corrected for the known experimental moment of trans-2,3-dibromo-norbornylane.[6]

(5) Y. K. Syrkin and M. E. Dyatkind, Structure of Molecules and the Chemical Bond, Interscience Publishers (1950) p. 215.

(6) H. Kwart and L. Kaplan, This Journal, 75, 0000 (1953).

preparation? A tabulation of all other possible dibromo anhydrides that would possess the observed reactions 2,3 of the three isomers is contained in Table II together with their calculated dipole moments.

The limits of inaccuracy in our dipole moment measurement is estimated to be ±0.1D. The structure dipole moment values (Table I) calculated from individual bond moments are not corrected in all cases for mutual polarizability of the bonds and internal field interaction effects.[7] We estimate from the magnitude of

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(7) I. F. Holverstadt, W. D. Kumler, J. Amer. Chem. Soc., 64, 2988 (1942). R. J. W. LeFevre, Dipole Moments, Menthuen and Co., London, Chap. III (1948).

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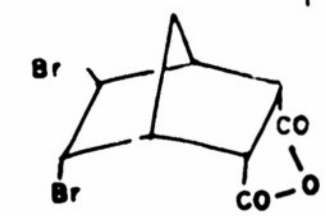
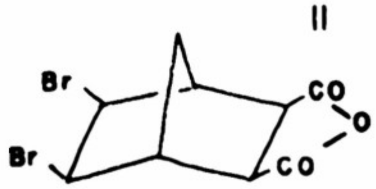
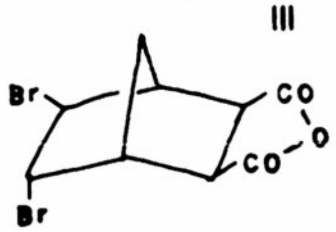
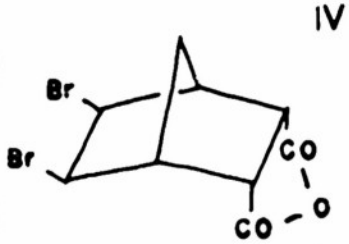
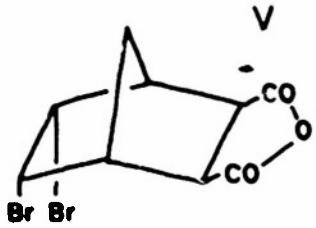
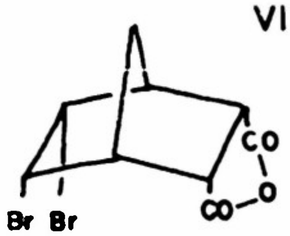
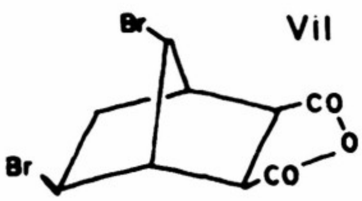
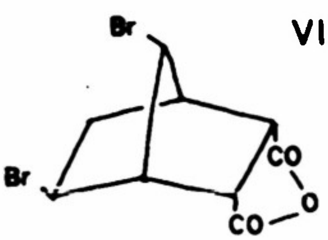
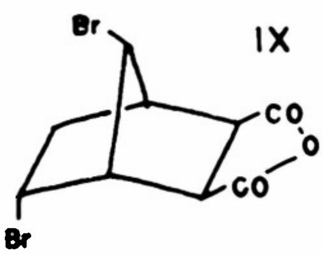
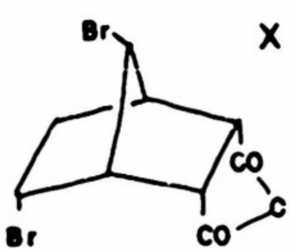
such effects that we have encountered in similar molecules[6] a maximum correction of ± 0.3D. It is seen, therefore, that the upper limit of discrepancy between calculated and observed moments is ± 0.4D.

The observed moment of compound A is noted in Table II to be in agreement with five possible structures whose calculated dipole moments are within the estimated limits of discrepancy. On the other hand the observed dipole moments of compounds B and C correspond well to a single structure in each case. It seems reasonable by considering the mechanism of formation and the possibilities therein for

TABLE II

Calculated and Observed Moments of all Possible Structures

Dibromo Anhydride Structure	μ_D calculated	μ_D observed in agreement		
		A	B	C
I 	6.1			
II 	4.4	4.5		
III 	2.5			2.3
IV 	4.3	4.5		

V 	4.4	4.5		
VI 	8.6			
VII 	4.5	4.5		
VIII 	4.5	4.5		
IX 	3.0		3.0	
X 	6.0			

rearranged products[8] ignored by the previous authors[2,3] to reconcile

(8) W. E. Doering, Abstracts, 113th Meeting of the American Chemical Society, April 19-23, 1948, Chicago, Illinois, p. 44. T. P. Neville, E. DeSala and C. L. Wilson, J. Chem. Soc., 1188 (1939). c.f. also reference (10).

the dipole moment data with the structural assignments for compounds B and C and make a consistent choice among the possibilities for the structure of compound A.

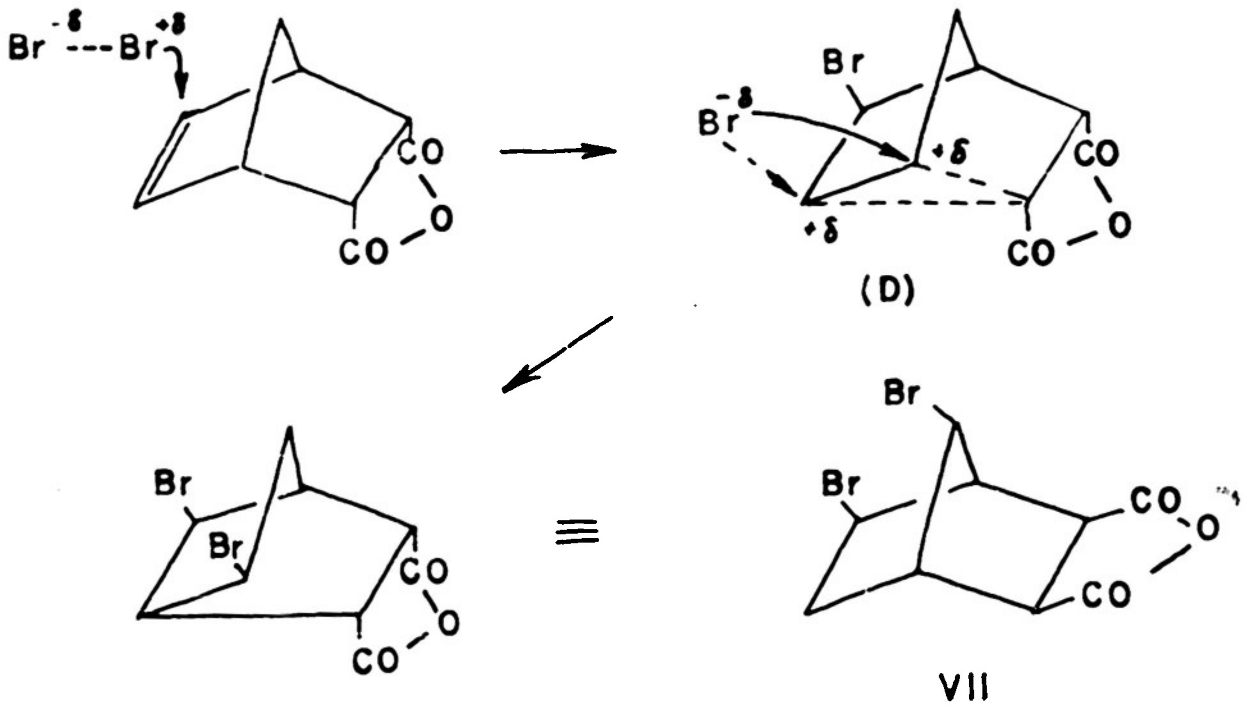
Thus the addition of bromine to the <u>endo</u> cyclopentadiene-maleic anhydride adduct would, in terms of the modern concept[9] of

(9) M. J. S. Dewar, Electronic Theory of Organic Chemistry, Oxford, 1949, p. 141 et seq.

this reaction type, involve primary attack of an electrophilic bromine fragment on the double bond and consequent formation of a bridged cation intermediate[10] as pictured in equation (1).

(10) For a comprehensive discussion of entirely analogous cases see S. Winstein et al, This Journal, <u>74</u>, 11 (1952), and reference (11b).

That the initial attack on the double bond occurs at the <u>exo</u> side as represented above is consonant with many analogous observations in the stereochemistry of addition to multiple bonds in



EQUATION I

bicyclic systems.[11] Stabilization of the bridged cation complex D

(11) (a) K. Alder and G. Stein, Ann., 515, 191 (1935); Ann., 525, 183 (1936).
(b) H. Kwart, This Journal, 75, 0000 (1953).

would be expected to occur by trans displacement of the delocalized electron pair by the accompanying halogen anion. It is of interest that the steric course of the reaction is in keeping with observations[11b] on the analogous chlorination of pinene. Displacement at the dotted arrow site would result in the unrearranged structure IV whereas displacement at the other site would lead to the structure VII indicated. Both IV and VII are consistent with the dipole moment data. Preference for the rearranged structure over the unrearranged IV is dictated by many demonstrations of rearranged products on addition to the double bond in related bicyclic systems, e.g., the observations of Bartlett and Schneider[4] on the addition of halogen in dicyclopentadiene and the results of bromination of norbornylene in this laboratory.[6] Furthermore only structures VII and IV lead reasonably and by means of well known analogous reactions in bicyclic systems to the unique structure IX consistent with the observed moment of compound B. A profound rearrangement of the sort necessary to explain the formation of structure IX on treatment of structure IV with acid appears to have no analogy in previous observations. However, treatment of VII with strong acid (HBr) at high temperature would be expected[6] to promote the establishment of bornyl-isobornyl halide equilibrium[12] known to favor the bornyl

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(12) H. Meerwein and K. von Emster, Ber., 55, 2500 (1922).

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configuration. Equation (2) represents this acid catalyzed isomerization.

We picture this as a concerted solvolysis[13] and surmise

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(13) C. G. Swain, This Journal, 70, 1119 (1948).

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that since a moderate amount of HBr is eliminated in a side reaction, the halogen acid is functioning as the electrophilic reagent as well as the source of nucleophilic reagent (Br^-). The considerably greater inertness in solvolytic reactivity of halogen on the methylene bridge[14] apparently prevents a similar inversion at the 7 position.

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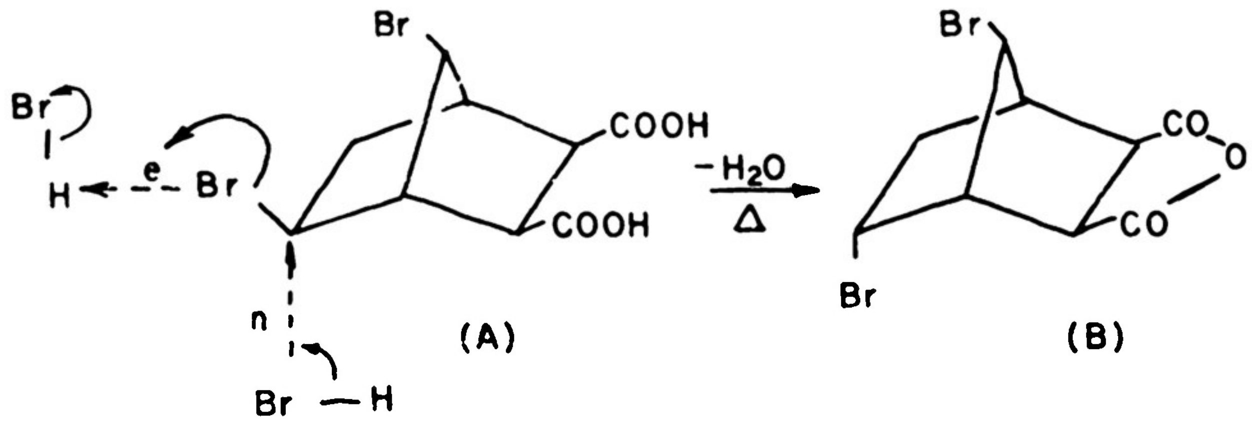
(14) J. D. Roberts, W. Bennet and R. Armstrong, This Journal, 72, 3329 (1950).

The formation of an unrearranged product, structure III, on bromination of the *exo*-cyclopentadiene-maleic anhydride adduct would imply that a bridged ion intermediate similar to that postulated above for addition to the *endo* adduct does not obtain in bromination of the *exo* configuration and the normal *trans* course of halogen addition to a double bond occurs. A pertinent observation has been made by



EQUATION 2

Bartlett and Barnes[15] in their studies of the solvolysis of the

(15) P. D. Bartlett, Abstracts of the Twelfth National Organic Chemistry Symposium of the American Chemical Society, Denver, Colorado, June 12-15, 1951, p. 6.

2-tosylates of dihydrodicyclopentadiene. These authors have shown that greater assistance from participation of the neighboring bond in formation of a bridge cation intermediate is afforded the isomer in which the substituent ring is fused to the bicycloheptane system in the *endo* configuration.

Chart II is a summary of the structural assignments deduced from the foregoing considerations.

Experimental:[16]

(16) All melting points given are uncorrected and were taken with a hot stage microscope.

Preparation of *endo*-3,6-Methylene-1,2,3,6-tetrahydro-*cis*-phthalic Anhydride (the *endo* adduct): The procedure of Diels and Alder[17] was followed using one mole of freshly distilled cyclopentadiene and one mole of maleic anhydride. The product was recrystallized from low boiling petroleum ether. A 95 per cent yield of the *endo* adduct (m.p. 161-62°)[17] was obtained.

(17) O. Diels and K. Alder, Ann., 460, 98 (1928).

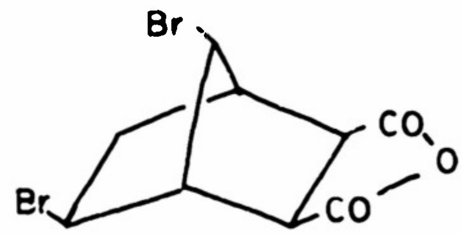
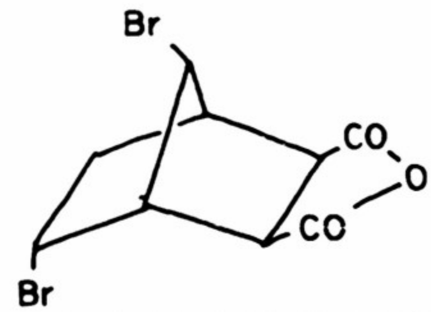
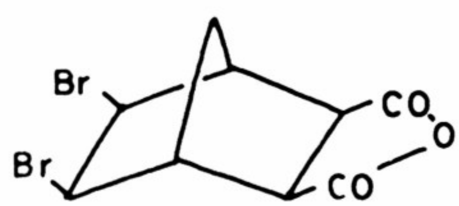
Compound	m. p.	Structure confirmed in this paper
A	209°	
B	249°	
C	184°	

CHART II

Bromination of the *endo*-adduct: The procedure of Bartlett and Schneider[4] was followed. From 0.1 mole (16.4 g.) of the *endo*-adduct and 0.12 moles (19.2 g.) of bromine there was obtained 22 grams (68 per cent) of the dibromoanhydride, m.p. 205-6°.

Preparation of *endo*-3,6-Methylenehexahydro-*cis*-phthalic Anhydride: The procedure of Bartlett and Schneider was followed. From 0.1 mole (16.4 g.) of the *endo*-adduct there was obtained 14.4 grams (87 per cent) of the completely saturated compound (m.p. 165-67°).

Preparation of *exo*-3,6-Methylene-1,2,3,6-tetrahydro-*cis*-phthalic Anhydride (the *exo* adduct): The procedure of Craig[2] was followed. One mole (164 g.) of the *endo*-adduct was heated in an open flask immersed in an oil bath at 190±2° for 1.5 hours as measured by a thermometer immersed in the reaction mixture. Some material was lost due to sublimation. The brown cake that remained on cooling was taken up in 500 cc. of boiling benzene and boiled with 3 grams of norit. The filtered solution yielded 35 grams of crystalline material (m.p. 122-26°) when cooled to room temperature. Concentration of the filtrate produced an additional 12.6 grams of crystals (m.p. 112-17°). The two crops of crystals were combined and recrystallized from 200 cc. of benzene, yielding 30.7 grams of the *exo*-adduct (m.p. 139-41°).

Bromination of the exo-adduct: The procedure followed was that of Bartlett and Schneider.[4] From 0.1 mole of the exo-adduct and 0.12 moles of bromine there was obtained 22 grams (68 per cent) of the dibromoanhydride, m.p. 189-89.5°.

Preparation of exo-3,6-Methylenehexahydro-cis-phthalic Anhydride: The procedure of Bartlett and Schneider[4] was followed. From 0.1 mole of the exo-adduct there was obtained 13.3 grams (80 per cent) of the completely saturated compound (m.p. 85-6°).

Hydrolysis of the dibromoanhydride (m.p. 205-6°): The anhydride was hydrolyzed according to the procedure of Alder and Stein.[3] One tenth of a mole (32.4 g.) of the dibromoanhydride yielded 32 grams (94 per cent) of the dicarboxylic acid (m.p. 181-2° dec.).

Preparation of the dibromoanhydride (m.p. 248-49°): The procedure of Bartlett and Schneider[4] was followed. Twelve grams of the dibromoacid (m.p. 181-82°) yielded 3.2 grams of the dibromo-anhydride (m.p. 248-49°).

Determination of the dipole moments of the various adducts: The apparatus used in determining the capacitance of the various solutions was similar to that of Smyth and Stranathan.[18] A 1000

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(18) (a) G. L. Lewis and C. P. Smyth, J. Chem. Phys., 7, 1085 (1939).
(b) J. Stranathan, Rev. Sci. Instruments, 5, 334 (1934).

cycle hummer was used to determine the null point when taking readings.

Dioxane used as a solvent in the determinations was technical grade which was refluxed over sodium for a minimum of two days and then distilled from sodium as needed. The fraction boiling at 101.5° was used in this work. The benzene used in one determination was obtained by distilling thiophene-free benzene from sodium. The fraction boiling at 80-80.5° was taken.

Calculations of the dipole moments from the dielectric constant and refractive index data in Table III were done by the Guggenheim method of initial slopes.[19]

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(19) See reference 11b for further references and discussion.

Acknowledgement

The authors wish to express their gratitude and appreciation for the generous support of this work by the Office of Naval Research.

Table III

Dipole Moment Data for the Various Isomers

exo-3,6-Methylenehexahydro-*cis*-phthalic anhydride: $S^o = 0.027$ $\mu = 4.9D$

Conc. (moles/cc. x 10^5)	ϵ	n^2	$\epsilon - n^2$
0.00	2.2175	2.0161	0.2014
2.29	2.2805	2.0173	0.2632
4.16	2.3318	2.0181	0.3137
7.58	2.4221	2.0190	0.4031
9.63	2.4777	2.0198	0.4579

endo-3,6-Methylenehexahydro-*cis*-phthalic anhydride: $S^o = 0.027$ $\mu = 4.8D$

Conc. (moles/cc. x 10^5)	ϵ	n^2	$\epsilon - n^2$
0.00	2.2145	2.0167	0.1978
2.21	2.2845	2.0175	0.2670
4.50	2.3453	2.0187	0.3266
6.86	2.4093	2.0192	0.3901
9.90	2.4915	2.0201	0.4714

exo-adduct dibromide (m. 183-4°): $S^o = 0.006$ $\mu = 2.3D$

Conc. (moles/cc. x 10^5)	ϵ	n^2	$\epsilon - n^2$
A. Data . . . (Δ)			
0.00	2.2165	2.0170	0.1995
3.06	2.2372	2.0190	0.2182
5.52	2.2549	2.0207	0.2342
7.62	2.2718	2.0221	0.2497
9.26	2.2825	2.0239	0.2586
B. Data . . . (O)			
0.00	2.2194	2.0170	0.2024
2.23	2.2350	2.0187	0.2163
4.31	2.2488	2.0201	0.2287
6.70	2.2684	2.0215	0.2469
8.92	2.2849	2.0232	0.2617

Table III (Continued)

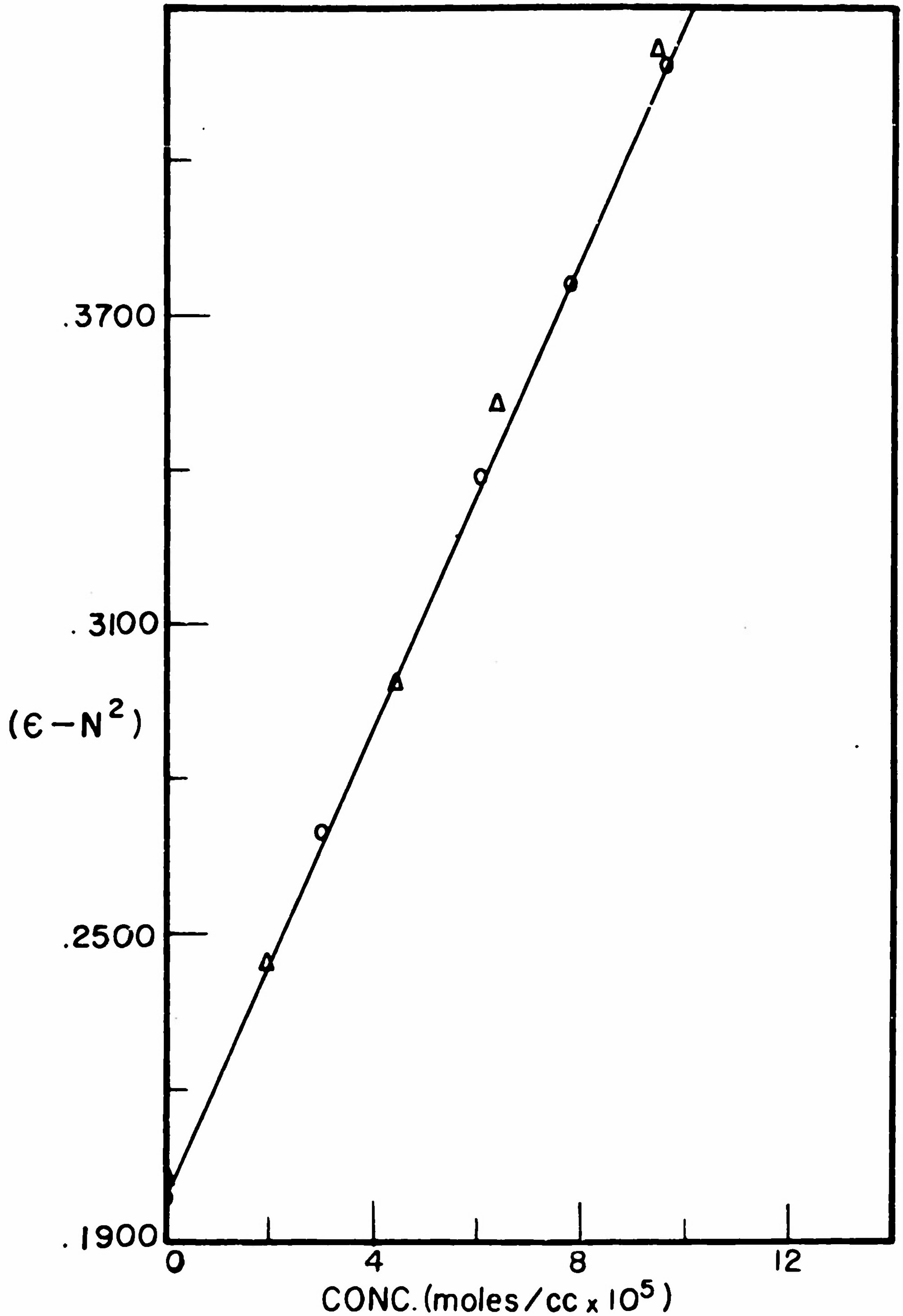
Dipole Moment Data for the Various Isomers

endo-adduct dibromide (m. 209°-): $S^{o} = 0.023$ $\mu = 4.5D$

Conc. (moles/cc. x 10^5)	ϵ	n^2	$\epsilon - n^2$
A. Data . . . (O)			
0.00	2.2164	2.0175	0.1989
3.01	2.2908	2.0204	0.2704
6.02	2.3614	2.0224	0.3390
7.79	2.4010	2.0244	0.3766
9.58	2.4454	2.0261	0.4193
B. Data . . . (△)			
0.00	2.2194	2.0170	0.2024
1.89	2.2635	2.0187	0.2448
4.38	2.3185	2.0201	0.2984
6.50	2.3749	2.0218	0.3531
9.35	2.4470	2.0244	0.4226

Dibromoanhydride (m. 249-50°): $S^{o} = 0.012$ $\mu = 3.2$ D

Conc. (moles/cc. x 10^5)	ϵ	n^2	$\epsilon - n^2$
0.00	2.2135	2.0170	0.1965
2.73	2.2461	2.0192	0.2275
4.69	2.2708	2.0207	0.2501
6.98	2.3002	2.0227	0.2776
10.40	2.3433	2.0258	0.3175



Guggenheim Plot for Compound A

Fig I

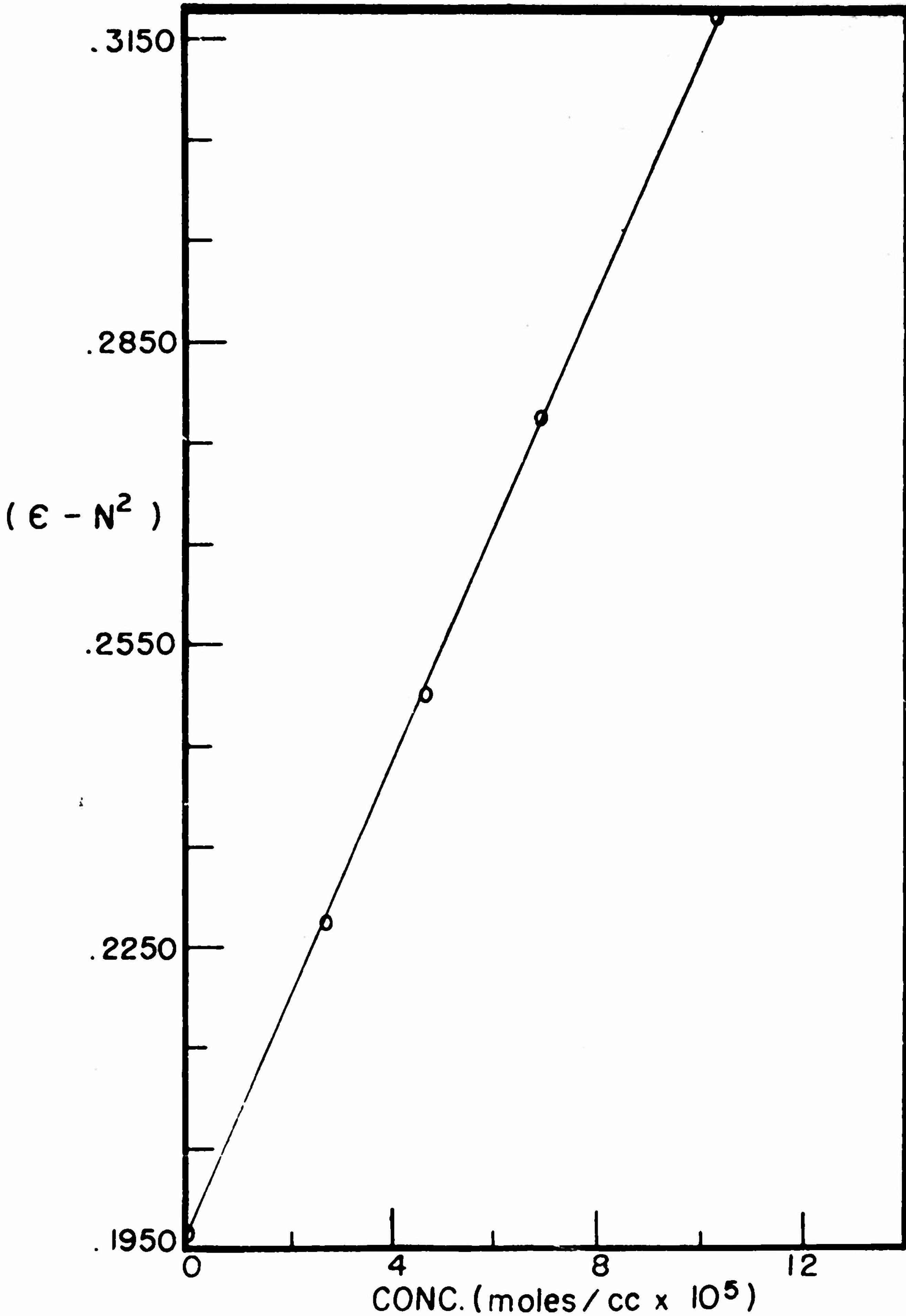
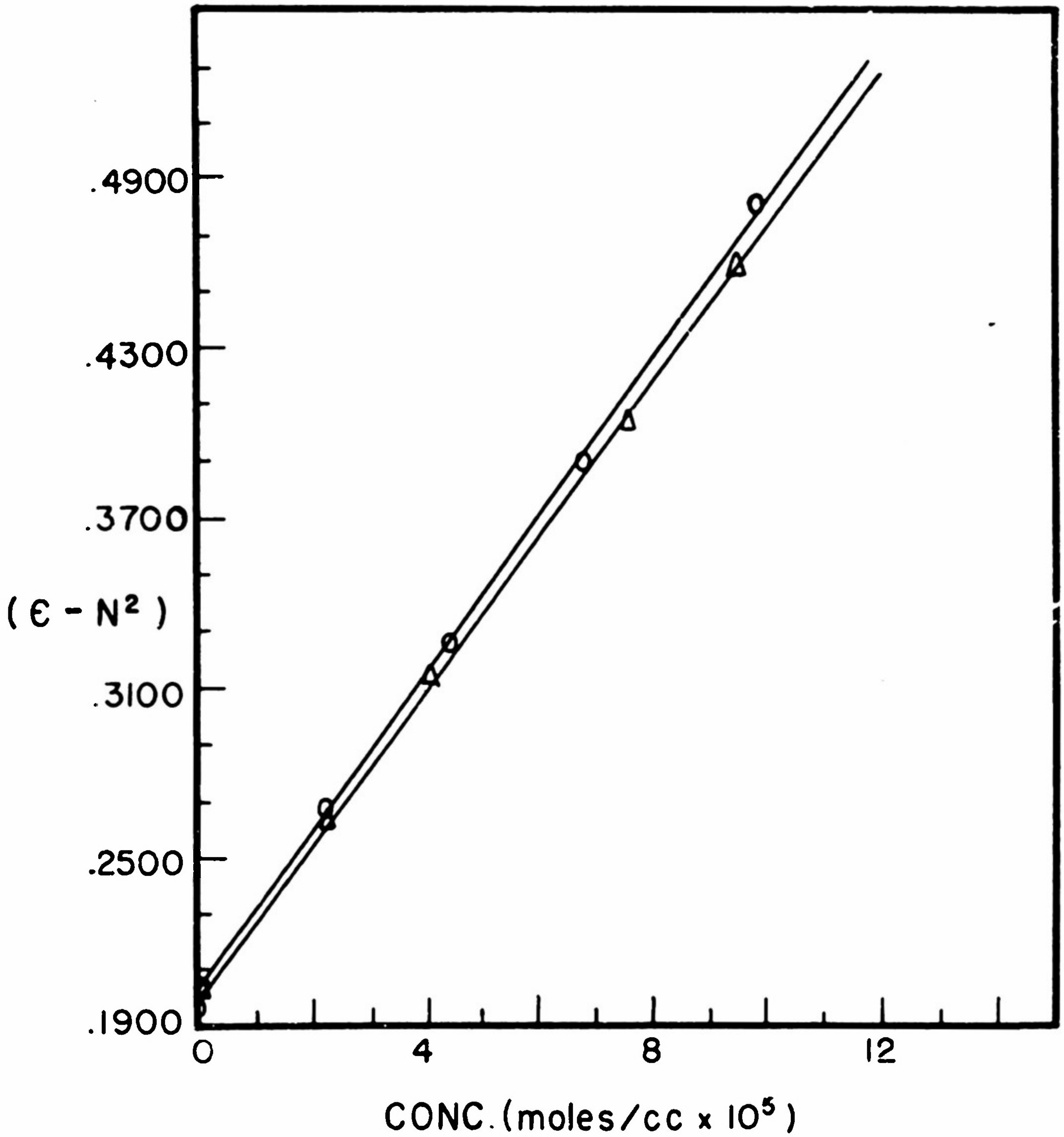


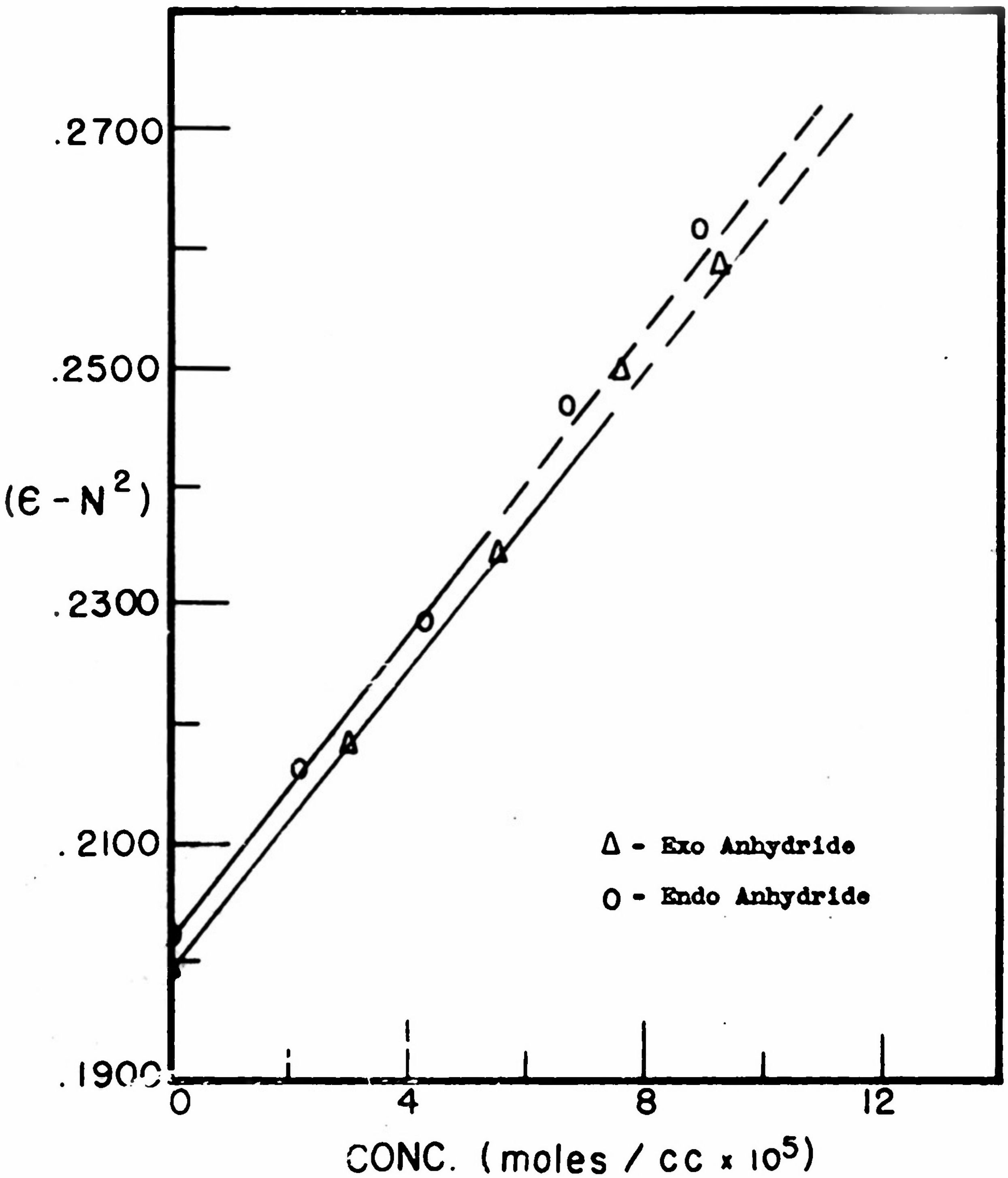
Fig II

Guggenheim Plot for Compound B



Guggenheim Plot for Compound C

Fig III



Guggenheim Plots for 3,6-Endo-methylenehexahydro-cis-phthalic Anhydride

Fig IV