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Phase Transitions In Bicyclic Compounds

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Phase Transitions In Bicyclic Compounds

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The study of a wide variety of organic structures by differential scanning calorimetry reveals that bicyclic caged compounds frequently possess a pre-melting phase transition. These compounds are characterized by low entropies of fusion (less than 21 j/K, mole) and relatively large entropies of transition. Derivative structures have been investigated and it has been found that substituents such as the anhydride, nitrile, and carbonyl groups retain the polymorphic phase properties of the parent ring systems while groups such as the imide, methylimide, and carboxylic acid exclude the appearance of a disordered solid phase. The phase properties of chloro and hydroxyl derivatives investigated are more varied and depend on the position of these groups on the ring. The variety of compounds studied shows that hysteresis is a common occurrence in all of these ring systems.

I. INTRODUCTION

Many bicyclic three-dimensional caged compounds are known to possess an orientationally disordered solid phase (formerly termed plastic phase) characterized by a high degree of motional freedom about certain molecular axes. The entropy of fusion is typically small and is less than 21 j/K, mole in the original classification of Timmermans'.[1] Examples include camphor, isoborneol, norbornene, bicyclo(2.2.2.)octene, and adamantane.[2-7] The occurrence of a pre-melting phase transition in these compounds is directly tied to their globular molecular shape which somehow minimizes the imtermolecular potential between lattice sites. Force constants in the orientationally disordered (ODIC) solid phase are two orders of magnitude less than those observed for non-polymorphic covalent and ionic solids thus permitting the lattice sites to assume other allowed orientations.[8] However, the occurrence of a free-rotator phase, as in methane above 20.4 K,[9] is not possible due to repulsive interactions from overlapping van der Waals clouds of neighboring lattice sites.

The transition process in these compounds is thermodynamically first-order in the Ehrenfest sense and is characterized by: 1) the calorimetric transition scan spanning up to 10 K depending on the heating rate of the instrument;[5] 2) a volume increase between 4–11% that reflects a substantial latent heat differential between the brittle and disordered solid phases;[10] and 3) a real hysteresis effect that is independent of the heating rate of the instrument.

II. SURVEY OF STRUCTURAL TYPES

A detailed literature survey reveals that compounds possessing a phase transition in the solid state share common properties such as sublimation and relatively high melting points compared to structurally related non-polymorphic compounds. However, not all compounds with these characteristics are polymorphic. A non-planar molecular shape seems to be a general requirement for an ODIC phase to be observed. Relatively few aromatic and heteroaromatic compounds evidence a solid state phase transition, the exceptions being pyromellitic dianhydride (PMDA) (Table II), 2,3-dimethyl-1,4-naphthaquinone,[11] and s-triazine,[12] but these compounds have small entropies of transition compared to the fusional entropy. For planar molecules the magnitude of the intermolecular potential has been shown to increase when elongation occurs along one molecular dimension. Fyfe[13] has noted this trend in the series benzene, naphthalene, and anthracene where the activation energy for in-plane molecular reorientation is 4, 21, and 100 kcal/mole respectively.

Small cyclic rings such as furan[14] and 2-imidazolidone (Table II) possess motionally disordered high temperature lattices. The introduction of a heteroatom into the ring system has two consequences. First the molecular symmetry lowering is important because even when the energy barrier for reorientation can be attained at temperatures below fusion, motion between symmetry related wells produces no contribution to the specific heat of the system.[4] Second, the incorporation of the heteroatom raises the melting point of the solid through hydrogen bond formation and electrostatic ordering forces, especially with the presence of oxygen and nitrogen. However, when more than one heteroatom is present in the ring as in hexamethylenetetramine, barriers to molecular reorientation may become too large and render the solid brittle until fusion.[15]

The three-dimensionality of the bicyclic ring system coupled with its globular molecular shape produces a situation where many orientations are accessible to the lattice sites. The consequence is the occurrence of an ODIC phase in ring systems such as bicyclo(2.2.1.)heptane, bicyclo(2.2.2.)octane, and trimethylbicyclo(2.2.1.)heptane. The parent unsubstituted structures provide an opportunity to study functional group effects on ODIC phase properties. Derivative compounds are readily available and easily tested for the presence of a phase transition by differential scanning calorimetry. Due to the variety of rings studied hysteresis and ring elongation effects were also considered.

III. RESULTS AND DISCUSSION

The thermal properties of the bicyclic and cyclic compounds studied by differential scanning calorimetry are given in Table II. Substitution on the bicyclic ring system by the anhydride, nitrile, and carbonyl groups retains the ODIC phase properties of their unsubstituted analogues in all cases studied. These functional groups increase the strength of the interaction between molecules in the lattice as shown by a rise in the enthalpy and temperature of transition and fusion compared to the parent structures. Table I summarizes the data for the anhydrides.

TABLE I

Comparison of Unsubstituted Bicyclic Rings With Bicyclic Anhydrides

		Transition Temperature (K)	Enthalpy Of Transition (j/g)	Ref.
1.	Norbornene	129	51.5	3
	NBA-5	365.3	95.4	
2.	Bicyclo(2.2.2.)octene	176	42.3	3
	BCOA-5	382.9	102.1	
3.	(±)-Camphor	206	125.1	5
	(±)-Camphoric Anhydride	375.4	95.0	
4.	(+)-Camphor	242	105.4	5
	(+)-Camphoric Anhydride	404.4	107.1	

NBA-5 = 5-norbornene-endo-2,3-dicarboxylic anhydride.
BCOA-5 = bicyclo(2.2.2.)-hept-5-ene-endo-2,3-dicarboxylic anhydride.

TABLE II

Thermal Properties Of ODIC Compounds and Related Structures

	T_{tr}(K)	ΔH_{tr}(j/g)	T_f(K)	ΔH_f(j/g)	ΔS_{tr}(j/K, m)	ΔS_f(j/K, m)
1. 5-norbornene-endo-2,3-dicarboxylic anhydride (NBA-5)	365.3	95.4	435.4	23.0	42.7	8.8
2. bicyclo(2.2.2.)-oct-5-ene-endo-2,3-dicarboxylic anhydride (BCOA-5)	382.9	102.1	419.2	25.5	47.3	8.8
3. trans-2,3-dicyanobicyclo(2.2.1.)-hept-5-ene (DCBCH-5)	339.1	119.1	370.8	18.0	51.0	7.1
4. 8,10-dioxaquadracyclo(2.2.1.0.2)undecane-9,11-dione (DOQUD)	481.8	89.1	536.4	23.0	33.5	7.5
5. cis-2,3-dichlorobicyclo(2.2.1.)-hept-5-ene-endo-2,3-dicarboxylic anhydride	339.1	77.0	457.6 d	23.0	52.7	11.7
6. 1,4,5,6,7,7-hexachlorobicyclo(2.2.1.)-hept-5-ene-endo-2,3-dicarboxylic anhydride	385.4	28.7	506.0	7.2	27.6	5.4
7. pentacyclo(5.4.0.0^{2,6}.0^{3,10}.0^{5,9}.)undecane-9,11-dione (PUD)	365.9	184.5	516.8	22.6	87.9	7.5
8. (+)-camphoric oxime	384.5	86.6	393.3	12.6	37.7	5.4
9. (+)-camphoric anhydride	404.4	107.1	493.6	31.0	48.1	11.3
10. (±)-camphoric anhydride	375.4	95.0	493.9	31.4	46.0	11.7
11. 3,3,4,4-tetracyanobicyclo(2.2.2.)-oct-5-ene (TCBCO-5)	476.7	90.8	533.2	21.8	32.6	7.1
12. 3-oxa-1,8,8-trimethyl-(±)-bicyclo(2.3.1.)-octan-4-one	N.O.	N.O.	487.9	28.5	N.O.	9.6
13. 2-imidazolidone	344.0	38.0	397.3	59.4	9.6	13.0
14. 8,8,9,9-tetracyanoquadracyclo(2.2.1.0^{3,5}.2.)nonane (TCQCN)	425.8	18.8	467.9 d	65.7	9.6	31.0
	462.1	1.7			0.8	
15. caffeine	420.8	8.8	508.3	107.9	4.2	41.4
16. triethanolamine borate	466.7	23.4	499.4	45.2	7.9	14.2
17. pyromellitic dianhydride (PMDA)	505.9	15.5	558.9	148.5	6.7	58.2
18. cis-2,3-di(hydroxymethyl)bicyclo(2.2.1.)-hept-5-ene	N.O.	N.O.	353.0	111.3	N.O.	43.5
19. 4-cyclohexene-cis-1,2-dicarboxylic anhydride (CHA-4)	N.O.	N.O.	371.6	106.7	N.O.	47.7

N.O. = not observed

Anhydride Derivatives

Four types of anhydride ring structures have been studied belonging to the bicyclo(2.2.1.)heptene, bicyclo(2.2.2.)octene, trimethylbicyclo(2.3.1.)octane, and the cyclic ring system of 4-cyclohexene-cis-1,2-dicarboxylic anhydride (CHA-4). The structures are shown in Figure 1. Amongst the series only CHA-4 does not exhibit a pre-melting anomaly in the specific heat, having an entropy of fusion of 43.5 j/K, mole. In this case the criteria of sublimation and similarity of functional group with the bicyclic compounds fails to predict a phase transition for the cyclic structure. This is one of many examples where a small change in structure or atom substitution has a pronounced effect on phase properties.

Comparison of the three bicyclic ring systems reveals little difference in the thermodynamic quantities for the anhydrides. The slightly lower heat of transition for NBA-5 of 15.61 kj/mole compared to 18.16 kj/mole for bicyclo(2.2.2.)-oct-5-ene-endo-2,3-dicarboxylic anhydride (BCOA-5) may result from unfavorable *H–H* interactions that occur at the bridgehead position in the former compound, although no relationship between ring strain and phase properties has been found. Significant, however, is the increased entropy of fusion for the camphoric anhydrides in relation to NBA-5 and BCOA-5. The greater amount of order persisting into the ODIC phase of the bicyclo(2.3.1.) ring system seems to be inherent to the ring structure because the contribution of the freely rotating methyl groups should increase the disorder in the high temperature lattice.

Lactones

The reduction of one of the carbonyl groups of (±)-camphoric anhydride produces the monolactone 3-oxa-1,8,8-trimethyl-(±)-bicyclo(2.3.1.)-octan-4-one, an ODIC solid with an entropy of fusion of 9.6 j/K, mole. This compound has not been quantitatively studied below the fusion point but its waxy appearance at ambient temperature and low entropy of fusion indicates that a phase transition occurs below 293 K, the lowest temperature instrumentally attained in the study. The loss of an ordering group such as the carbonyl gives rise not only to a more disordered high temperature lattice, compared to the anhydride, but the weakened intermolecular forces depress the transition temperature. Conversely, the presence of a heteroatom in the ring as in the dilactone, 8,10-dioxoquadracyclo(2.2.1.0.2.)-undecane-9,11-dione (DOQUD), raises the transition temperature to 481.6 K.

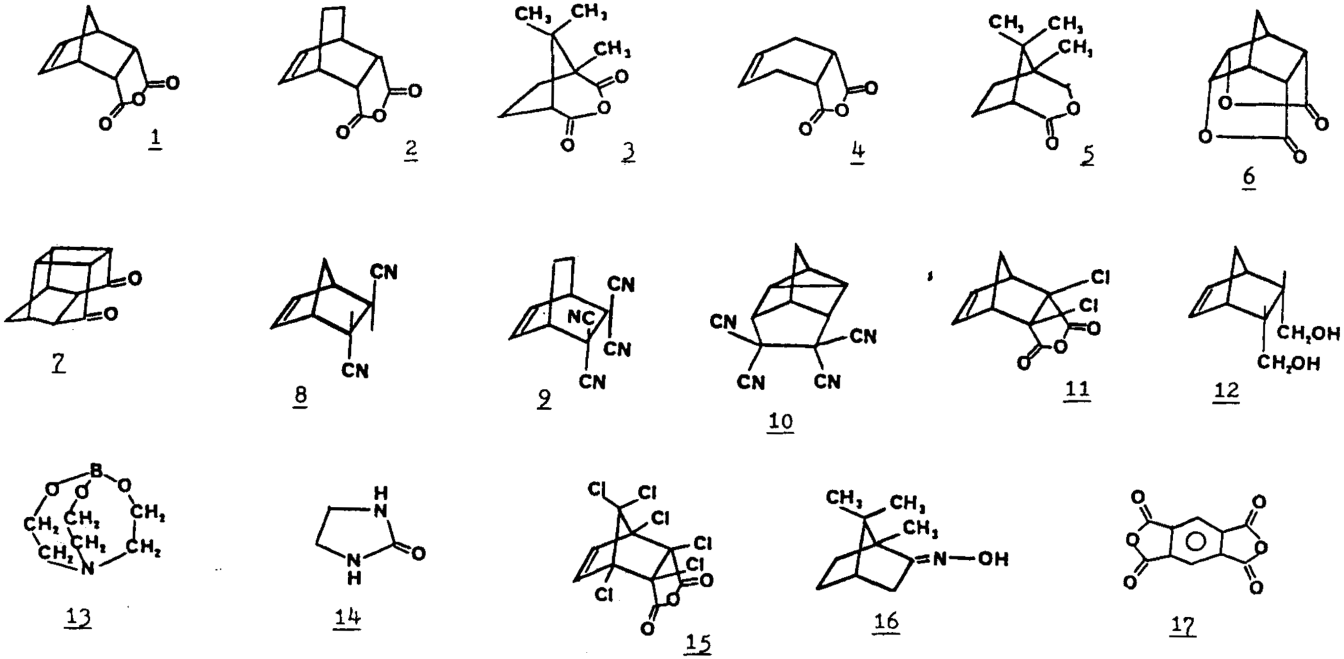

FIGURE 1 Structures of Compounds in Table II. NBA-5 (1), BCOA-5 (2), Camphoric anhydride (3), CHA-4 (4), 3-oxa-1,8,8-trimethyl-(±)-bicyclo(2.3.1.)-octan-4-one (5), DOQUD (6), PUD (7), DCBCH-5 (8), TCBCO-5 (9), TCQCN (10), DCBCHA-5 (11), Cis-2,3-di(hydroxymethyl)bicyclo(2.2.1.)-hept-5-ene (12), Triethanolamine borate (13), 2-Imidazolidone (14), 1,4,5,6,7,7-hexachlorobicyclo(2.2.1.)-hept-5-ene-endo-2,3-dicarboxylic anhydride (15), Camphoric oxime (16), PMDA (17).

Ring elongation effects

An elongation of the ring system has been shown by Clark *et al.*[2] to increase the forces between lattice sites as the molecule deviates from a spherical shape. There seems to be a point reached in the elongation along one molecular dimension where maximum values for the thermodynamic quantities are attained. Beyond this the intermolecular forces become too strong and hinder the onset of the ODIC phase. Pentacyclo(5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.)-undecane-9,11-dione (PUD) is an example where the presence of a second bicyclic ring raises the enthalpy of transition to 32.10 kj/mole. With the introduction of a fourth ring into the norbornene framework to give tetracyanoquadracyclo(2.2.1.$0^{3,5}$.2.)nonane (TCQCN), the entropy of fusion rises to 31.0 j/K, mole and the solid can no longer be considered as ODIC in the Timmermans' sense. Further deviation from sphericity would eventually yield a non-polymorphic compound with reorientational and translational degrees of freedom gained simultaneously at the fusion point to an isotropic liquid.

Nitrile group

Like the anhydride function the nitrile group retains polymorphic phase properties in a molecular framework conducive to its occurrence. Trans-2,3-dicyanobicyclo(2.2.1.)-hept-5-ene (DCBCH-5) and 3,3,4,4-tetracyanobicyclo(2.2.2.)-oct-5-ene (TCBCO-5) are ODIC solids that exhibit slightly more globular shapes than the corresponding anhydrides. Both nitriles have entropies of fusion of 7.1 j/K, mole. An added feature of the nitrile derivatives is a higher heat of transition on a per gram basis than for any other functional group studied. This is particularly true for DCBCH-5 with a transitional enthalpy of 119.5 j/g.

Chloro group

Chlorine substitution on the bicyclic anhydride ring system has pronounced effects on the thermal properties depending on the position of the substituents. Cis-2,3-dichloro-bicyclo(2.2.1.)-hept-5-ene-endo-2,3-dicarboxylic anhydride (DCBCHA-5) is an ODIC solid with an entropy of fusion of 11.7 j/K, mole. The reduction in the transition temperature from 365.3 K for NBA-5 to 339.1 K can be traced to a weakening of the intermolecular forces due to the bulky chlorine groups. This effect has also been observed in the chlorinated benzenes.[16] Cis halogen addition across the double bond of NBA-5, giving cis-5,6-dichlorobicyclo(2.2.1.)-heptan-endo-2,3-dicarboxylic anhydride and cis-5,6-dibromobicyclo(2.2.1.)-heptan-endo-2,3-dicarboxylic anhydride completely eliminates the polymorphic phase properties. Apparently steric crowding in these positions on the ring produces large repulsive barriers to molecular reorientation, essentially confining the molecules to very few orientations below the melting point.

Hydroxyl group

Only one hydroxy compound, cis-2,3-di(hydroxymethyl)bicyclo-(2.2.1.)-hept-5-ene, was investigated and this proved to be non-polymorphic. The high entropy of fusion of 47.7 j/K, mole is probably due to the elongation of the ring system by the substituents. The relatively low melting point of 354.6 K compared to the ring diol, cis-2,3-dihydroxy-bicyclo-(2.2.1.)-hept-5-ene, fusing at 459 K,[17] argues against the occurrence of intermolecular hydrogen bonding in the former compound.

Imide, methylimide, and carboxylic acid

Replacement of the anhydride functional group in NBA-5 with the imide, methylimide, and carboxylic acid results in a brittle solid with a high entropy of fusion and no evidence of a transition in the solid state. These substituent groups hinder the reorientational process by increasing intermolecular contacts through hydrogen bond formation. Hence, 5-norbornene-endo-2,3-dicarboximide, N-methyl-5-norbornene-endo-2,3-dicarboximide, and 5-norbornene-endo-2,3-dicarboxylic acid are non-polymorphic solids.

Cooling studies

Calorimetric cooling studies were performed on some of these orientationally disordered bicyclic compounds in order to investigate the phenomenon of hysteresis, common to first-order phase processes. The data is given in Table III.

No overall trend in hysteresis for the various structural bicyclic ring systems can be discerned from the data. The difference between the transition temperature in the heating and cooling cycles is in part due to the experimental conditions employed, with temperature differences between cycles increasing as the scanning rate of the instrument

TABLE III

Cooling Studies of ODIC compounds

		Transition Temperature (K) Heating	Cooling
1.	NBA-5	365.5	351.4
2.	BCOA-5	382.9	N.O. at 315
3.	DCBCHA-5	339.1	N.O. at 315
4.	DCBCH-5	339.1	N.O. at 315
5.	(+)-Camphoric Anhydride	404.4	399.4
6.	(±)-Camphoric Anhydride	375.4	343.0
7.	(+)-Camphoric Oxime	385.4	347.0
8.	PUD	365.9	N.O. at 315

N.O. = not observed

increases. However, very slow heating and cooling rates of 1–2 degrees/hour have shown that hysteresis is an inherent property of these systems. Dilatometric measurements[10] on (±) and (+)-camphoric anhydride, 2-imidazolidone, and triethanolamine borate through the phase transition reveal that the transition temperature in the cooling cycle is always lower than in the heating mode, varying from 5 K for 2-imidazolidone to 23 K for (±)-camphoric anhydride. The large variation in the data from both the DSC and dilatometric sources points to a process that is related to the large displacements the molecular centers of mass experience on transition to the disordered phase. This behavior is in contrast to systems having a second-order phase transition where the magnitude of the hysteresis effect is relatively small with the volume change at the transition point typically about 1%. The dependence of cooperative phenomena on the degree of molecular motion can also be seen in the study of mixed systems. Because short-range correlations are more extensive below the transition point in systems exhibiting first-order thermodynamics[18] impurity effects on the thermal properties have been found in general, to be more severe[19] than in systems with a λ transition. For example, the low temperature phase diagram of the CH_4/CD_4 system exhibits almost ideal behavior over the entire composition range[9] while that of camphor[5] shows the presence of eutectics at the reorientational transition point.

While all of the compounds listed in Table III are subject to some amount of hysteresis the transition point reappears at the same temperature after a fusion cycle in all cases except for DCBCHA-5 and PUD. The former compound probably decomposes via a retrograde Diels–Alder reaction but is cyclable if initially heated through the transition point only. After one heating of PUD past 365.9 K reheating gave the phase transition at 347.0 K with the enthalpy reduced to about one-tenth of its original value. The polymorphic phase properties are completely eliminated if the compound is heated once past fusion. At this time no explanation can be advanced for this behavior.

IV. CONCLUSIONS

A survey of three-dimensional caged structures by differential scanning calorimetry has found that many of the parent and substituted compounds are polymorphic in contrast to aromatic molecules. Derivative structures such as the anhydride, nitrile, and carbonyl frequently retain an ODIC phase with increased temperatures and enthalpies of transition compared to the unsubstituted compounds for most cases studied. Conversely the presence of the imide, methylimide, or carboxylic acid groups prevents the occurrence of an ODIC phase through intermolecular hydrogen bond formation which results in large barriers to molecular reorientation. This behavior has also been evidenced in certain hydroxy derivatives and in compounds where heteroatoms are present in the ring system as in hexamethylenetetramine.

In addition the study showed that hysteresis effects are prominent in first-order phase transitions and vary unpredictably between structurally similar molecules. The property is inherent to the thermodynamic order of the transition process although it is somewhat affected by the cooling rate of the instrument.

V. EXPERIMENTAL

All melting and transition temperatures were determined using the Perkin-Elmer DSC-1B instrument operated in the active heating mode at scan rates of 1.25 and 2.50 degrees K/minute. Cooling studies were conducted at 1.25 degrees K/minute. In all runs the sensitivity of the instrument was 2 millicalories/second at a full scale deflection of 10 mv. Temperature calibration was performed using standards obtained from the Fischer Scientific Company and the U.S. National Bureau of Standards. All samples and calibration standards were run in sealed aluminum sublimator pans. The heat of fusion of indium was taken as the standard in the enthalpy determinations with peak areas integrated by a planimeter. The reported temperatures and enthalpies are mean values of at least three different samples. Temperature values are precise to ±1.3 K, with a relative uncertainty in the enthalpy of ±0.26 j/g.

VI. EXPERIMENTAL PREPARATIONS

Most procedures were based on well established literature methods with purification accomplished by vacuum sublimation unless otherwise stated.

1. NBA-5, (+)-camphoric oxime, (+) and (±)-camphoric anhydride, 1,4,5,6,7,7-hexachlorobicyclo(2.2.1.)-hept-5-ene-endo-2,3-dicarboxylic anhydride, 2-imidazolidone, triethanolamine borate, PMDA, and caffeine were purchased from Aldrich Chemical Company and purified by repeated sublimations.

2. Pentacyclo(5.4.0.$0^{2,6}$.$0^{3,10}$.$0^{5,9}$.)undecane-9,11-dione. The compound was obtained from Dr. W. W. Zajac Jr., prepared according to the literature.[20]

3. 4-Cyclohexene-cis-1,2-dicarboxylic anhydride. The compound was prepared by the method of Hatch.[21] m. 371.6 by DSC (lit. 374 K).

4. N-methyl-5-norbornene-endo-2,3-dicarboxylic anhydride. The method of Cookson[22] was followed by refluxing a solution of 10g of 5-norbornene-endo-2,3-dicarboxylic anhydride (0.06 moles) and 100 mls of 40% aqueous methylamine for 20 hours. After removal of the excess methylamine 30 mls of acetyl chloride was added to the solid with the evolution of heat accompanying the dissolution. Evaporation of the liquid gave a white solid. m. 379–382 K by DSC.

Analysis: C = 67.75%, H = 6.34%, N = 7.60%;
Calculated for $C_{10}H_{11}NO_2$: C = 67.42%, H = 6.74%, N = 7.87%.

5. 5-Norbornene-endo-2,3-dicarboximide. 48g of NBA-5 (0.3 moles) was refluxed 5 hours in 250 mls of concentrated NH_4OH according to Worrall.[23] m. 454 K by DSC (lit. 455 K).

6. 5-Norbornene-cis-endo-2,3-dicarboxylic acid- The diacid was prepared by the hydrolysis of NBA-5.[24] m. 458–9 K (lit. 459 K).

7. Cis-2,3-dichlorobicyclo(2.2.1.)-hept-5-ene-endo-2,3-dicarboxylic anhydride. 13 mls of freshly distilled 1,3-cyclopentadiene was added dropwise to a stirred solution of 25g of dichloromaleic anhydride dissolved in 95 mls of benzene at room temperature. After two hours a white solid had precipitated. m. 468–70 K (lit 466 K).[25]

Analysis: C = 46.36%, H = 2.51%, O = 21.09%, Cl (by difference) = 30.04%.
Calculated for $C_9H_6O_3Cl_2$: C = 46.35%, H = 2.58%, O = 20.60%, Cl = 30.47%.

8. Cis-5,6-dichlorobicyclo(2.2.1.)heptane-endo-2,3-dicarboxylic anhydride. The compound was prepared according to the method of Masson (26). m. 446 K by DSC (lit. m. 449 K).

9. Cis-5,6-dibromobicyclo(2.2.1.)heptane-endo-2,3-dicarboxylic anhydride. The compound was prepared by mixing solutions of 25g of NBA-5 in 100 mls of chloroform with 8.5 mls of bromine in 100 mls of chloroform according to Hendrickson.[27] Illumination of the mixture with a 90 watt bulb initiated a vigorous reaction after 2 min. Precipitation of a white solid ensued and this was recrystallized twice from ethyl acetate. 25g of the cis-dibromoanhydride was recovered for a 50.8% yield. m. 483-5 K by DSC (lit. 483-4 K).

10. 8,10-dioxaquadracyclo(2.2.1.2.2.)undecane-9,11-dione. 25g of the cis-dibromoanhydride was dissolved in 75 mls of water and 200 mls of acetone.[27] Evaporation of the solution to 150 mls gave a white solid on cooling. 20g of the diacid were recovered for a 76% yield. The diacid was neutralized by the addition of a 2N KOH solution until a final pH of 9.1 was obtained. Evaporation of the liquid gave a white solid which was placed in a sublimator and pyrolyzed under vacuum at 200 C. Some solid sublimed and this was then resublimed at 100 C in vacuum. m. 536.4 K by DSC (lit. 539 K). IR in a KBr pellet: 1790 cm^{-1} (broad); Proton N.M.R. in d_6-acetone: four peaks of equal area at 4.78δ, 3.45δ, 3.05δ, and 1.97δ.

Analysis: C = 60.26%, H = 4.50%, O = 35.24%.
Calculated for $C_9H_8O_4$: C = 60.00%, H = 4.48%, O = 35.52%.

11. 8,8,9,9-tetracyanoquadracyclo(2.2.1.$0^{3,5}$.2.)nonane. The reaction of 1,4-norbornadiene with tetracyanoethylene in benzene was performed according to the literature.[28] The recovered solid was recrystallized three times from ethyl acetate and sublimed in vacuum at 100 C. m. 461 K d by DSC (lit. 457-458 K).

Analysis: C = 71.01%, H = 3.73%, N = 25.41%.
Calculated for $C_{13}H_8N_4$: C = 70.90%, H = 3.66%, N = 25.44%.

12. 3-oxa-1,8,8-trimethyl-(±)-bicyclo(2.3.1.)-octan-4-one. A solution of 18g of sodium borohydride in diglyme was added dropwise to a

solution containing 18g of (±)-camphoric anhydride and 14g of $AlCl_3$ in 70 mls of diglyme under a nitrogen flow at 0 C. The rate of addition of the borohydride was controlled by the nitrogen flow, with the temperature of the solution kept below 40 C. After the addition was complete the reaction mixture was allowed to warm to room temperature, stirred an additional 16 hours, and then quenched by pouring the solution into a beaker containing 80 mls of conc. HCl and 700g of ice. The acidic solution was evaporated to 200 mls with the white precipitate collected and neutralized by a 0.3N NaOH solution. The alkaline filtrate was evaporated to a waxy solid by vacuum distillation and placed in a soxhlet extractor with 250 mls of benzene for 24 hours. Evaporation of the benzene gave a waxy solid which readily sublimed at 100 C in vacuum. m. 487.8 K by DSC (Table II). IR of a KBr pellet: 1730 cm^{-1}. ^1H in CCl_4: three methyl peaks at 0.9δ, 1.05δ, and 1.88δ, all of which are doublets.

Analysis: C = 71.60%, H = 9.08%, O = 18.54%.
for $C_{10}H_{16}O_2$: C = 71.43%, H = 9.52%, O = 19.05%.

13. Trans-2,3-dicyanobicyclo(2.2.1.)-hept-5-ene. The compound was prepared by the Diels-Alder reaction of fumaronitrile[29] and 1,3-cyclopentadiene in ethanol at O C.[30]

Analysis: C = 74.79%, H = 5.50%, N = 20.02%.
Calculated for $C_9H_8N_2$: C = 75.00%, H = 5.56%, N = 19.44%.

14. Bicyclo(2.2.2.)-oct-5-ene-endo-2,3-dicarboxylic anhydride. The compound was prepared according to the method of Diels and Alder[31] by reacting 1.33g of 1,3-cyclohexadiene to a stirred solution of 1g of maleic anhydride in 15 mls of diethyl ether at 0 C.

Analysis: C = 67.75%, H = 6.34%, O = 25.92%.
Calculated for $C_{10}H_{10}O_3$: C = 67.42%, H = 6.74%, O = 25.84%.

15. 3,3,4,4-tetracyanobicyclo(2.2.2.)-oct-5-ene. 0.5g of tetracyanoethylene (0.04 moles) was dissolved in a solution of 50 mls of ethanol/10 mls benzene. To the stirred solution at room temperature was added dropwise 0.5 mls of freshly distilled 1,3-cyclohexadiene. After 5 minutes a white solid had precipitated. m. 541–3 K (with decomposition) by DSC. IR of a CsI pellet: 2240 cm^{-1} (s), 1685 cm^{-1} (s).

Analysis: C = 69.23%, H = 3.85%, N = 26.92%.
Calculated for $C_{12}H_8N_4$: C = 69.30%, H = 3.86%, N = 26.89%.

16. Cis-2,3-di(hydroxymethyl)bicyclo(2.2.1.)-hept-5-ene. The reduction of NBA-5 with LAH was accomplished in THF at 0 C under a nitrogen flow. The slightly exothermic addition took twenty minutes with stirring continued for two hours at 0 C and for an additional hour at room temperature. The reaction was then quenched by the slow addition of 20 mls of a 3M HCl solution. The cool reaction mixture was extracted three times with 50 ml portions of diethyl ether, which were combined and then dried over anhydrous $MgSO_4$. Evaporation of the ether layer gave a white solid that was vacuumed dried. 13g of the solid was placed in a soxhlet extractor with 250 mls of benzene for 20 hours. Reducing the volume of the solvent to 90 mls precipitated the solid. Sublimation at 100 C at reduced pressure gave 10g of solid for a yield of 57%. m. by DSC 353–355 K. IR of a CsI pellet: 3300 cm^{-1} (broad) and no carbonyl band. ^1H in $CDCl_3$: five peaks at 6.05δ (quartet), 3.50δ (doublet of quartet), 2.80δ (singlet), 2.55δ (quartet), and 1.40δ (singlet) in a ratio of 1 : 2 : 1 : 1 : 1 respectively.

Analysis: C = 70.19%, H = 9.09%, O = 20.55%.
Calculated for $C_9H_{14}O_2$: C = 70.13%, H = 9.09%, O = 20.78%.

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