ride. Evaporation of the extract *in vacuo* produced a dark residue which upon treatment with hot hexane left a purple solid (77 mg). The hexane solution was chromatographed on silica gel. Elution with increasing amounts of ether–hexane gave (1) a red material (30 mg), (2) **32** (47 mg, 16%), and (3) **18** (45 mg, 30%), respectively. The red product on further chromatography on silica gel using 5% benzene in hexane yielded **33** (24 mg, 16%) and **34** (6 mg, 4%). The structures of **18, 32, 33,** and **34** were assigned upon comparison with authentic samples or spectral data of such samples.

Dione **32** is a yellow solid: ir (KBr) 6.0, 6.25, 6.9, 7.5, 7.7, 7.9, 10.35, 10.9, 12.8, 13.0, and 13.6 μ; nmr ($CDCl_3$, 100 MHz) δ 7.15–8.3 (m, 12 H, aromatic), 6.3 (s, 1 H, olefinic), and 4.5 (s, 1 H, 9-fluorenyl).

Anal. Calcd for $C_{23}H_{14}O_2$: C, 85.70; H, 4.38. Found: C, 85.42; H, 4.36.

(*Z,Z*)-2,5-Bis(*N*-benzoylimino)-7,7-diphenylbicyclo[4.1.0]hept-3-ene (36). A benzene solution (45 ml) of **35** (1.88 g, 6.0 mmol) and **2** (1.32 g, 7.0 mmol) was refluxed for 3 hr. The white amorphous precipitate was filtered and vacuum sublimed to give 1,4-phenylene-*N,N'*-dibenzoylamine (0.16 g, 8%), mp 338–340° (lit.[14] mp >300°). The filtrate was concentrated and subjected to preparative tlc over Merck Kieselgel GF 254 with benzene–hexane (1:1) elution. The band with R_f 0.5,[15] extracted with chloroform, gave a pale yellow oil which slowly solidified. Recrystallization from benzene–hexane gave **36** (1.87 g, 65%): mp 264°; ir (KBr) 6.05 (C═O), 6.2, 6.8, 7.6, 7.8, 8.0, 8.5, 9.4, 12.4, and 14.4 μ; nmr ($CDCl_3$) δ 7.9–8.2 (m, 4 H, aromatic), 7.1–7.7 (m, 16 H, aromatic), 6.39 (s, 2 H, olefinic), and 2.78 (s, 2 H, cyclopropyl).

Anal. Calcd for $C_{33}H_{24}N_2O_2$: C, 82.47; H, 5.13; N, 5.83. Found: C, 82.57; H, 5.40; N, 5.71.

Registry No.—**1**, 1050-82-4; **2**, 883-40-9; **4**, 42976-05-6; **5**, 832-80-4; **8**, 42976-06-7; **9**, 42976-07-8; **10**, 42976-08-9; **11**, 42976-09-0; **12**, 42976-10-3; **13**, 43021-10-9; **14**, 42976-11-4; **15**, 42976-12-5; **16**, 42976-13-6; **17**, 106-51-4; **18**, 130-15-4; **21**, 42976-14-7; **22**, 42976-15-8; **23**, 42976-16-9; **24**, 42976-17-0; **25**, 42976-18-1; **30**, 42976-19-2; **31**, 42976-20-5; **32**, 42976-21-6; **33**, 746-47-4; **35**, 16720-35-7; **36**, 42976-23-8.

References and Notes

(1) We should like to acknowledge support of this research by (a) the donors of the Petroleum Research Fund, administered by the American Chemical Society, the National Science Foundation, and the National Institutes of Health, and (b) the New Zealand Universities Grants Committee.

(2) For a review see B. Halton, *Chem. Rev.*, **73,** 113 (1973).

(3) A Mustafa and M. Kamel, *J. Amer. Chem. Soc.*, **75,** 2934 (1953).

(4) Arocyclopropenes **3, 6,** and **7** may be named (a) 2,5-bis(*N*-phenylsulfonylamino)-1,1-diphenyl-1*H*-cyclopropabenzene (**3**), (b) 2,7-bis(*N*-phenylsulfonylamino)-1,1-diphenyl-1*H*-cyclopropa[*b*]naphthalene (**6**), and (c) 2,7-bis(*N*-phenylfulfonylamino)-spiro[1*H*-cyclopropa[*b*]naphthalene-1,9'-fluorene] (**7**), respectively.

(5) Minor products from **1** and from **4** with **2** are tetraphenylethylene (<10%) and benzophenone azine (<10%).

(6) The structure of **11** is based on its analysis, nmr and ir spectra (see Experimental Section), and origin. The stereochemistry of **11** is not known.

(7) The mechanisms of isomerization and the temperature dependence of the nmr of *N*-benzenesulfonylimines are discussed by M. Raban, E. Carlson, and F. Jones, *Chem. Commun.*, 1235 (1969). For further discussion and leading references concerning isomerization of imines, see R. Moriarty, C. Yeh, K. Ramey, and P. Whitehurst, *J. Amer. Chem. Soc.*, **92,** 6360 (1970).

(8) (a) L. F. Fieser and M. A. Peters, *J. Amer. Chem. Soc.*, **53,** 4080 (1931); (b) L. Horner and E. Lingnau, *Justus Liebigs Ann. Chem.*, **591,** 21 (1955); (c) N. Latif, I. Zeid, and N. Mishriky, *J. Prakt. Chem.*, **312,** 209 (1970).

(9) F. M. Dean, P. G. Jones, R. B. Morton, and P. S. Sidisunthorn, *J. Chem. Soc.*, 5336 (1963).

(10) In **24** the hydrogen at C-3 of the acenaphthenone moiety is not shielded by the cyclohexenedione unit; a fused benzene ring as in **25** is necessary to effect the shielding. Similarly the hydrogen at C-1 in the fluorene moiety of **16** is not shielded whereas it is in the benzo analog **22**.

(11) R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," 2nd ed, Wiley, New York, N. Y., 1970, p 122.

(12) D. C. F. Law and S. W. Tobey, *J. Amer. Chem. Soc.*, **90,** 2376 (1968).

(13) In these experiments **33** and fluorenone azine were also formed (<10%).

(14) R. Adams and J. L. Anderson, *J. Amer. Chem. Soc.*, **72,** 5154 (1950).

(15) Bands with R_f 0.7 and 0.9 gave benzophenone azine (15%) and tetraphenylethylene (3%), respectively.

Benzocyclopropenes *via* Reactions of *p*-Quinonebenzenesulfonimides with Diphenyldiazomethane: a Reinvestigation. Quinone Imide Isomerism[1]

A. G. Pinkus* and J. Tsuji

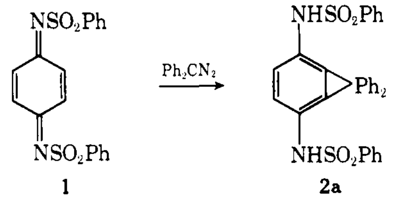
Department of Chemistry, Baylor University, Waco, Texas 76703

Received July 18, 1973

The product from the reaction of *p*-quinonedibenzenesulfonimide (**1**) and diphenyldiazomethane does not have the benzocyclopropene structure (**2a**) as reported by Mustafa and Kamel. On the basis of conclusive ir and ^1H nmr studies, the correct structure in solution and in the crystalline state is that of a novel substituted biocyclo[4.1.0]-3-heptene (**2b**). Two types of crystals (higher melting tablets and lower melting needles) were isolated from *p*-quinonedibenzenesulfonimide prepared by the oxidation of *p*-phenylenedibenzenesulfonamide by lead tetraacetate. The two forms are identified as syn and anti isomers (**1a** and **1b**, respectively) on the basis of moderate differences in melting point and ir spectra and marked differences in behavior on standing.

According to a recent review on benzocyclopropenes,[2] the two earliest reports claiming syntheses of benzocyclopropenes were in 1930 by De and Dutt[3] and in 1953 by Mustafa and Kamel;[4] neither of these reports has been substantiated or refuted in a published paper. Mustafa and Kamel[4] claimed that substituted benzocyclopropenes (*e.g.*, **2a**) were formed in reactions of diphenyldiazomethane with *p*-quinonebenzenesulfonimides (*e.g.*, **1**). Halton[2] cast doubt on the structures assigned to these products as well as to that in the analogous reaction between **1** and 9-diazofluorene on the basis that recent attempts by Halton and Milsom[5] to obtain 7,7-diphenylbenzocyclopropenes led to the isolation of fluorene derivatives.

Because of the importance of benzocyclopropene as a unique structure, we undertook a study of the reaction of



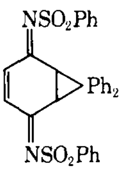
1 2a

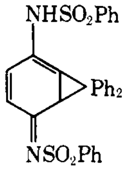
p-quinonedibenzenesulfonimide with diphenyldiazomethane. Recent interest in this topic as indicated by the above reports[2,5-7] prompts us to present our earlier work[8] at this time, since our results should serve to clarify certain aspects of benzocyclopropene chemistry as presently reported in the literature.

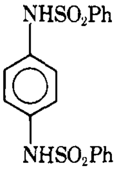
During the course of the investigation, two different crystal forms of *p*-quinonebenzenesulfonimide (1) were isolated from the oxidation *p*-phenylenedibenzenesulfonamide. This work leading to the proposed identification of the two forms as syn and anti isomers is also reported.

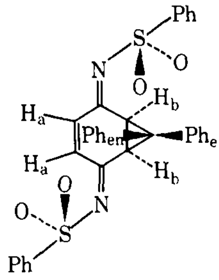
Results and Discussion

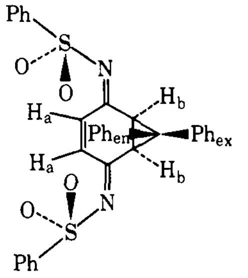
The Mustafa-Kamel Compound. It appeared reasonable to us that the structure of the addition product from diphenyldiazomethane and *p*-quinonedibenzenesulfonimide (1) might be the bicyclic cyclopropane derivative (2b)[9] as would be expected for the first product following nitrogen elimination. Infrared spectra should easily be able to distinguish structures 2a and 2b, since the spectrum of the proposed benzocyclopropene (2a) would be expected to possess N-H stretching bands similar to those in *p*-phenylenedibenzenesulfonamide (3) whereas the spectrum of the cyclopropane derivative 2b would have C=N stretching bands as in *p*-quinonedibenzenesulfonimide (1). The spectrum of an intermediate type of structure (2c) between 2a and 2b would be expected to show both N-H and C=N stretching bands.

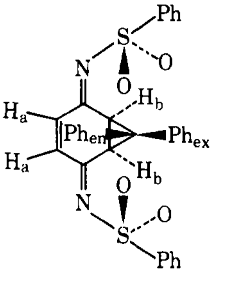

2b


2c


3


2d


2e


2f

The ir spectra (which are reproduced in the thesis of J. T.) clearly show that the correct structure is 2b. The spectrum of *p*-phenylenedibenzenesulfonamide (3) showed a well-defined sharp N-H stretching band at 3180 cm^{-1}. The spectrum of *p*-quinonedibenzenesulfonimide (1) showed C=N stretching as a strong band at 1500 cm^{-1} with a shoulder at 1520 cm^{-1}. The spectrum of the addition product (2) showed no absorption in the N-H stretching region but possessed two strong C=N stretching bands at 1508 and 1538 cm^{-1}. The absence of N-H stretching eliminates structure 2c as well as 2a from consideration.

The shift in the C=N stretching frequencies is toward lower frequencies from the quinone imide 1 to compound 2 for both bands, *i.e.*, 1538 > 1520 cm^{-1} and 1508 > 1500 cm^{-1}. This shift is in the direction expected for greater conjugation in the quinone imide 1 than for 2b. Here the observation in the present work that compound 2 had a slight yellow color (after five recrystallizations) is consistent with the conjugation present in 2b but inconsistent with 2a.

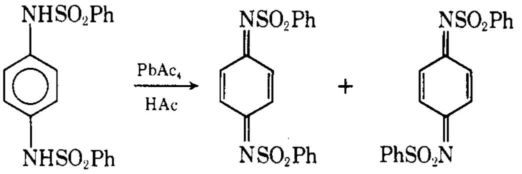
Mustafa and Kamel[4] reported that the addition product 2 was soluble in alcoholic potassium hydroxide; this was confirmed in the present investigation. In terms of structure 2b this acidity is readily explicable as a result of activation of the tertiary hydrogens of the cyclopropane ring α to the adjacent C=N groups, analogous to acidity of hydrogens in α positions relative to carbonyl groups. No studies were carried out to see whether the benzocyclopropene system could be generated by protonation on the nitrogens of the potentially ambident anion.

The nmr spectrum is also in accord with the bicyclo[4.1.0]-3-heptene structure (2b). The spectrum shows the bridgehead (H_b) and ring vinyl hydrogens (H_a) both as singlets at τ 5.70 and 3.74, respectively, with relative areas in a precise ratio of 1:1. The chemical shift for the bridgehead hydrogens[11] appears at lower field than has been reported[12] for bridgehead hydrogens in other bicyclo[4.1.0]heptanes, -heptenes, and -heptadienes. However, deshielding would be expected[18] from the C=N groupings which are allylic to both bridgehead hydrogens. Further deshielding of bridge hydrogens from the $PhSO_2$ grouping is also possible, as is discussed below in connection with isomerism of 2b. Absorption from the 20 phenyl hydrogens occurs in complex multiplets between τ 2.4-2.9 and 1.9-2.1. Since the latter areas are in the ratio of 3:1 (15:5), this indicated that one of the phenyl groups must be deshielded with respect to the other. From models, it would appear that the endo phenyl group (Ph_{en}) would be in the shielding zone of the π-electron cloud of the vinyl group and thus absorption from the endo phenyl hydrogens would occur at higher field than the exo phenyl hydrogens (Ph_{ex}); thus, tentatively, the latter are identified as being responsible for the multiplet absorption at the lowest field position.

Isomerism might be expected for the addition product 2b. The singlet observed for the vinyl ring hydrogens (H_a) at τ 3.74 and bridgehead hydrogens (H_b) at τ 5.70 clearly show that the $PhSO_2$ groups must be in a syn or cis configuration[19] with respect to each other; the anti or trans form[19] (2d) is excluded since two doublets would be expected. Two syn configurations are possible (2e and 2f). From possible steric interference between the $PhSO_2$ groups and the phenyl groups on the cyclopropane ring, one would expect conformation 2e with both $PhSO_2$ groups away from the cyclopropane ring to be the thermodynamically more stable form. The nmr data appear to indicate, however, that form 2f with both $PhSO_2$ groups on the same side as the cyclopropyl ring is the configuration of the product formed.[22] This conclusion is based[23] on the relatively high field position of the vinyl ring protons and low field position of the bridgehead hydrogens, as was discussed above. A definitive solution of this configurational question for the solid state should be possible by X-ray crystallography, since the compound exists as well-formed crystals.

In summary, the product from the reaction of *p*-quinonedibenzenesulfonimide (1) and diphenyldiazomethane was shown to have a novel bicyclo[4.1.0]-3-heptene structure (2b) and not the benzocyclopropene structure (2a) proposed by Mustafa and Kamel.[4] The work of De and Dutt[3] should also be checked; if this is also unsubstantiated, then the credit for the first two preparations of stable benzocyclopropene structures should go to Anet and Anet[24] and Vogel and coworkers.[25]

Quinone Imide Isomerism. The discovery of quinone imides as a new class of compounds by Adams and Nagarkatti[26] resulted in an intensive investigation of the preparation and properties of these interesting compounds by Adams and his students as published in over 50 papers.[27] During the preparation of *p*-quinonedibenzenesulfonimide by the procedure of Adams and coworkers,[26,28] for use in the investigation described above, two different crystal forms were observed during recrystallization from ethyl acetate. The two forms, a lower melting, flocculent yellow form and higher melting, yellow tablets, could be easily separated mechanically. It was suspected that these distinctly different crystalline forms might be syn (**1a**) and anti (**1b**) isomers.[29] The higher melting form was evidently the form obtained by Adams and coworkers. Elemental analysis established the same formula for the lower melting form. The infrared spectra (see Experimental Section) of the two crystalline forms, although qualitatively similar, showed distinct differences in frequency shifts of some bands, differences in relative band intensities, and the appearance of some bands in one spectrum and not in the other. Another observation was made which confirms the difference in the two types of crystals: on long standing in the absence of light, the higher melting form turned into a black form whereas the lower melting form was essentially unchanged in appearance. The new black substance, on being heated at about 130°, formed a more refractory material (see Experimental Section). The infrared spectrum of this material (before thermal conversion) was markedly different from that of either of the original isomers. In contrast the visually unchanged yellow lower melting form melted at a higher temperature than the original material but the melt did not solidify. This difference in physical and chemical behavior serves to reemphasize the reality of the difference between the two forms as well as to demonstrate that one form does not convert into the other in the solid state even on long standing. A definitive assignment of configuration cannot be made at present. Since well-formed crystalline forms are available, an X-ray diffraction study should be able to settle this question easily.[30]



1a, syn (cis or *Z*, *Z*)

1b, anti (trans or *Z*, *E*)

Experimental Section[32]

Preparation of *p*-Phenylenedibenzenesulfonamide (3). *p*-Phenylenedibenzenesulfonamide was prepared in 84% yield from *p*-phenylenediamine by the Schotten-Baumann procedure,[33] mp 246° (lit.[33] mp 247°).

Reaction of *p*-Quinonedibenzenesulfonimide (1) and Diphenyldiazomethane. Benzophenone hydrazone, mp 98-99° (lit.[34] mp 97-98°), was prepared[34] in 90% yield by the reaction of benzophenone and anhydrous hydrazine. The latter was prepared from 85% hydrazine hydrate and sodium hydroxide pellets. Benzophenone hydrazone was oxidized with mercury(II) oxide and the diphenyldiazomethane was treated directly with *p*-quinonedibenzenesulfonimide (1)[35] according to the procedure below, which differs from that of Mustafa and Kamel.[4] (In our hands their procedure was unsuccessful.) Mercury(II) oxide was prepared by adding a solution of 40 g (1.0 mol) of sodium hydroxide in 100 ml of water to a solution of 15 g (0.055 mol) of mercury(II) chloride in 500 ml of water. The yellow mercury(II) oxide which precipitated was washed with water several times by decantation, collected by filtration, and dried over calcium chloride, yield 10 g (83%).

Two grams (0.010 mol) of benzophenone hydrazone and 3.0 g (0.014 mol) of mercury(II) oxide were placed in 30 ml of petroleum ether (bp 30-50°) and shaken for 6 hr. A precipitate which formed was removed by filtration, and, on evaporation of solvent from the filtrate, a residue of 2.0 g of diphenyldiazomethane was obtained which crystallized on cooling with Dry Ice. One gram (0.051 mol) of diphenyldiazomethane was dissolved in 30 ml of dry benzene with 1.5 g (0.039 mol) of *p*-quinonedibenzenesulfonimide (1), which also dissolved. After refluxing for 3 hr, the dark-red solution became brown. A dark-brown residue was obtained on removal of solvent. After washing several times with cold ether, a yellow solid remained. By dissolving the solid in benzene and adding petroleum ether to the hot solution, yellow crystals of 2 were formed, 1.1 g (51%), mp 202-203° (lit.[4] 85%, mp 202°). After five recrystallizations, the compound still had a faint yellow color; however, the melting point was unchanged.

Preparation of *p*-Quinonedibenzenesulfonimide (1) and Isolation of Syn and Anti Isomers. Although the preparation by Adams and coworkers[26,28] was followed, the experimental procedure is given because of the isolation of two different crystalline forms in the past instance. Finely powdered *p*-phenylenedibenzenesulfonamide[26,28,33] (13.5 g, 0.035 mol) was suspended in 150 ml of glacial acetic acid, and 16 g (0.023 mol) of freshly prepared lead tetraacetate was added. The mixture turned yellow immediately and thickened after 30 min. In about 2 hr, the mixture became less viscous and yellow crystals were formed. After about 3.5 hr of stirring, a small amount of ethylene glycol was added to destroy excess lead tetraacetate. The yellow product was collected by filtration, washed with a small amount of acetic acid, and dried, yield 12.5 g (92.5%). The product was extracted with hot ethyl acetate, leaving some insoluble residue. After filtration, the residue was dissolved in another portion of ethyl acetate. Flocculent, light-yellow crystals, mp *ca.* 160°, were formed in the first extract. Yellow, crystalline tablets, mp 176-179° (lit.[26,28] mp 178-179°), separated from the second ethyl acetate solution.

On repeated recrystallization from ethyl acetate of the higher melting crystals, the two types of crystals, which could be clearly distinguished, were mechanically separated. The higher melting yellow tablets (in smaller amount) changed color at *ca.* 165° and melted at 176-178°. The flocculent yellow crystals changed color at 150° and melted at 163-165°. The latter were more soluble in organic solvents than the former. An analytical sample of the lower melting crystals was prepared by recrystallizing three times from ethyl acetate and drying *in vacuo* at 56°.

Anal. Calcd for $C_{18}H_{14}N_2O_4S_2$: C, 55.96; H, 3.66. Found:[36] C, 56.02; H, 3.62.

When an attempt was made to recrystallize some of the higher melting material (mp 176-179°) from benzene, a product, mp 168-172°, was obtained. This indicated that a separation could not be made with benzene, possibly because of isomer interconversion[37] resulting in a mixture of crystals being formed, lowering the melting point.

Thermal Behavior of the Aged Syn and Anti Isomers. When the samples from the original work were examined shortly before writing the present paper (*ca.* 16 years), all of the samples of the higher melting forms had turned black, the crystal form, however, still being apparently unchanged from the tablet form. The lower melting yellow, fluffy form was unchanged with respect to visual inspection. Some peculiar aspects of "melting point" behavior, however (as observed with a calibrated Fisher melting point block), became evident. On raising the temperature slowly for the previously higher melting tablets (not black), melting was not observed even above the melting point of the original material (166-168°). However, when the temperature was increased rapidly, or when crystals were placed on the preheated block, melting took place at temperatures ranging from 130 to 135° followed by resolidification of the melt at the temperature of melting. This melting and resolidification behavior was observed up to 160°. The new solid did not melt up to 240°. The thermal behavior was also studied with a Perkin-Elmer Model DSC-1B differential scanning calorimeter using sealed Al capsules under a nitrogen atmosphere at a temperature increase rate of 20°/min. A moderately broad endothermic peak centered at 126 ± 1 was observed; a structureless exothermic decomposition began at about 180°. This behavior is interpreted as a thermal conversion of the compound having mp *ca.* 130° to another compound or polymer having mp (if any) above 240°. The black material, as well as its thermal conversion product, were too insoluble in the usual nmr and ir solvents to be able to obtain spectra in solution. The nature of this new material was not investigated further, since this was outside the scope and purpose of the present concern. The yellow, fluffy crystalline isomer originally having the lower melting point (163–165°) and having the same appearance presently, now showed a melting point at about 180° whereas the melting point of *p*-benzenesulfonamide was unchanged after standing for the same period of time. In contrast to the other isomer, however, the melt did not resolidify even after cooling to room temperature or after standing for several days. With the differential scanning calorimeter, structureless exothermic decomposition began at about 160°. This markedly different chemical behavior is noted because it points up the fact that, even though the original melting points differ by only a few degrees, the differences in the isomers are real. Also these properties show that one form does not convert into the other even on long standing.

Infrared and Nmr Spectra. Infrared spectra of *p*-phenylenedibenzenesulfonamide (**3**), *p*-quinonedibenzenesulfonimide (**1**), and the addition product **2** were obtained as mineral oil mulls with a Baird ir spectrophotometer Model 4-55 and Perkin Elmer 337 instruments. Nmr spectra were obtained on deuteriochloroform solutions with tetramethylsilane as internal standard using a Varian DP-60 instrument.[38] Calibrations were made by a frequency side-band technique.

Because of problems in powdering the lower melting fluffy form of **1** for mull preparation, it was more difficult to obtain satisfactory mulls and therefore the two mulls are not exactly comparable with respect to relative band intensities. The lower melting form appeared to develop an electrical charge during the powdering process and would stick to the grinding surfaces. The main absorption bands (in cm^{-1}) were calibrated against polystyrene and are listed below in order of low melting material first followed by the corresponding band of the higher melting isomer. If no corresponding band is present, a dash is used to indicate absence of the band: C=C (aromatic) 1430 (sh), 1430 (sh, interference from mineral oil band); skeleton bend 1345 (m), 1325 (m, -), 1315 (m); C=N 1525 (w), 1520 (m), 1505 (m), 1500 (s); SO_2 1270 (s), 1258 (s, -), 1250 (s), 1110 (s), 1100 (s, -), 1112 (sh, PhS), 683 (s), 680 (s); others 1680 (w, -), 1186 (w, -), 1070 (m, -), 1040 (s), 1035 (s, -), 905 (m), 825 (s), 816 (s), 710 (w), 709 (m), 635 (s), 643 (s) (s = strong, m = medium, w = weak, sh = shoulder).

Acknowledgment. The authors acknowledge with appreciation the purchase of the ir Perkin-Elmer and differential scanning calorimeter instruments in part financed by grants from the National Science Foundation to the department.

Registry No. 1a, 43134-47-0; **1b**, 43134-48-1; **2f**, 42976-06-7; diphenyldiazomethane, 883-40-9.

References and Notes

(1) Based on M.S. thesis of J. T., Baylor University, 1957.

(2) B. Halton, *Chem. Rev.*, **73**, 113 (1973).

(3) S. C. De and D. N. Dutt, *J. Indian Chem. Soc.*, **7**, 537 (1930).

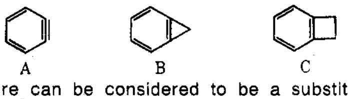
(4) A. Mustafa and M Kamel, *J. Amer. Chem. Soc.*, **75**, 2939 (1953).

(5) B. Halton and P. J. Milsom, unpublished observations in a footnote of ref 2. Halton also refers to the earlier unpublished Ph.D. Thesis by Baum[6] in which the structures assigned by Mustafa and Kamel[4] were reported to be incorrect.

(6) G. Baum, Ph.D. thesis, The Ohio State University, 1965; *Diss. Abstr. B*, **27** (1), 97 (1966).

(7) On contacting Dr. Harold Schecter, The Ohio State University, who directed Baum's thesis, and informing him of our work, he suggested that the papers be submitted for publication at the same time; the work of his group is being combined with that of Halton and his group in a joint paper.

(8) The work reported in the present paper was originally submitted in 1957 to *J. Amer. Chem. Soc.*; the recommendation of the referee was that the paper be rewritten for publication in *J. Org. Chem.* In the paper originally submitted (as in the thesis of J. T.) the significance of the position of benzocyclopropenes (B) in the sequence from benzynes (A) as unstable intermediates to the isolable benzocyclobutenes (C) was pointed out for the first time to our knowledge. At the time the question as to whether benzocyclopropenes would be stable enough for isolation had not yet been resolved. The only other later published reference to this point appears to be the paper by E. F. Ullman and E. Buncel, *J. Amer. Chem. Soc.*, **85**, 2106 (1963).



A B C

(9) The structure can be considered to be a substituted noncarene (bicyclo[4.1.0]-3-heptene) but is unique in that no other norcarenes having this type of structure have been previously described.[10]

(10) See below for references on bicyclo[4.1.0]heptane, -ene, and -diene systems.

(11) The substituted bicyclo[4.1.0]-3-heptene system (**2b**) is unique because of the double-bond substitutions at the 2 and 5 positions; no model systems of this type are available in the literature for close comparisons of positions of bridgehead hydrogens in the nmr spectra.

(12) A literature search on chemical shifts of bridgehead hydrogens in bicyclo[4.1.0]heptane systems revealed that accurate data on this is generally lacking because of the fact that, in the systems studied, there is coupling between bridgehead hydrogens and hydrogens in the 2, 5, and 7 positions, resulting in complex multiplets. Of the systems reported, chemical shifts of bridgehead hydrogens appear to be in the range τ 6.8–10.0 for bicyclo[4.1.0]heptanes,[13] 8.78 for a bicyclo[4.1.0]heptene,[14] and 6.12–6.88 for bicyclo[4.1.0]heptadienes.[15,16]

(13) D. Seyferth, H. Yamazaki, and D. L. Alleston, *J. Org. Chem.*, **28** 703 (1963); W. G. Dauben and G. H. Berezin, *J. Amer. Chem. Soc.*, **85**, 468 (1963); J. E. Hodgkins and R. J. Flores, *J. Org. Chem.*, **28**, 3356 (1963); W. G. Dauben and W. T. Wipke, *J. Org. Chem.*, **32** 2976 (1967); R. S. Boikess, M. Mackay, and D. Blithe, *Tetrahedron Lett.*, 401 (1971); J. Haywood-Farmer, H. Malkus, and M. A. Battiste, *J. Amer. Chem. Soc.*, **94**, 2209 (1972).

(14) A. D. Ketley, A. J. Berlin, E. Gorman, and L. P. Fisher, *J. Org. Chem.*, **31**, 305 (1966).

(15) E. Ciganek, *J. Amer. Chem. Soc.*, **87**, 652, 1149 (1965); E. Ciganek, *ibid.*, **89**, 1454 (1967); T. Mukai, H. Kubota, and T. Toda, *Tetrahedron Lett.*, 3581 (1967); M. Jones, Jr., *Angew. Chem., Int. Ed. Engl.*, **8**, 76 (1969); *Angew. Chem.*, **81**, 83 (1969); D. Schönleber, *Angew. Chem., Int. Ed. Engl.*, **8**, 76 (1969); *Angew. Chem.*, **81**, 83 (1969); see also W. von E. Doering and M. J. Goldstein, *Tetrahedron*, **5**, 53 (1959); R. Huisgen and G. Juppe, *Chem. Ber.*, **94**, 2332 (1961); C. Ganter and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 741 (1966).

(16) As early as 1964, Vogel and coworkers[17] showed the existence of fluxional equilibrium in a benzo-substituted bicyclo[4.1.0]heptene system by a variable-temperature nmr study. More recently, Dürr and Kober have shown that a spirobicyclo[4.1.0]heptadiene exists as an equilibrating system with spirocycloheptatriene. In the latter case the chemical shifts for the equilibrated bridgehead hydrogens are at values from τ 4.82 to 6.40 in deuteriochloroform: H. Durr and H. Kober, *Chem. Ber.*, **106**, 1565 (1973).

(17) E. Vogel, D. Wendisch, and W. R. Roth, *Angew. Chem.*, **76**, 432 (1964).

(18) Relatively low-field positions for bridgehead hydrogens in some 7,7-dicyanobicyclo[4.1.0]heptadienes as compared with other cyclopropanes were attributed by Ciganek[15] to deshielding by allylic and cyano groupings.

(19) According to IUPAC rules[20] as originated by the Chemical Abstracts group,[21] one of the syn or cis forms would be designated as the *Z,Z* configuration and the other as *E,E*; the anti or trans form would be designated *Z,E*. The suggestion of one of the referees on this is acknowledged.

(20) *J. Org. Chem.*, **35**, 2849 (1970).

(21) J. E. Blackwood, C. L. Gladys, K. L. Loening, A. E. Petrarca, and J. E. Rush, *J. Amer. Chem. Soc.*, **90** 509 (1968).

(22) This was pointed out by Dr. Schecter during a telephone conversation; the interpretation of nmr data is by the present authors and appears to be in agreement.

(23) A. G. Pinkus and C. D. Moon, unpublished work.

(24) R. Anet and F. A. L. Anet, *J. Amer. Chem. Soc.*, **86**, 525 (1964).

(25) E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Lett.*, 3625 (1965).

(26) R. Adams and A. S. Nagarkatti, *J. Amer. Chem. Soc.*, **72**, 4601 (1950).

(27) Paper 46 on quinone imides: R. Adams, L. M. Werbel, and M. D. Nair, *J. Amer. Chem. Soc.*, **80**, 3291 (1958). Paper no. 6 on quinol imide acetates: R. Adams and L. M. Werbel, *ibid.*, **80**, 5799 (1958).

(28) R. Adams and K. R. Eilar, *J. Amer. Chem. Soc.*, **73**, 1149 (1951).

(29) Although there is no ambiguity in the present case in the designation as syn and anti or cis and trans, respectively, IUPAC rules[20] can be used.

(30) One of the referees suggested that the work of Carlson, Jones, and Raban[31] be referred to in the discussion. It should be pointed out, however, that their work involved nmr studies in solution of the syn-anti isomerization of a substituted benzenesulfonamide. Nmr studies cannot be carried out on the solid forms and, as referred to below, studies indicate interconversion taking place in solution.

(31) E. Carlson, F. B. Jones, Jr., and M. Raban, *Chem. Commun.*, 1235 (1969).

(32) Melting points were determined with total immersion thermometers.

(33) O. Hinsberg, *Justus Liebigs Ann. Chem.*, **265**, 178 (1891).

(34) L. I. Smith and K. L. Howard in "Organic Syntheses," Collect. Vol. III, E. C. Horning, Ed., Wiley, New York, N. Y., 1955, p 351.

(35) Most of the work was done with the more soluble lower melting isomer, although no differences in results were observed with the higher melting isomer undoubtedly owing to the fact that interconversion takes place in solution (see below).

(36) Clark Microanalytical Laboratory, Urbana, Ill.

(37) More recent studies substantiate that interconversion occurs in solution at ambient temperatures: personal communication from Dr. Harold Schecter, The Ohio State University; A. G. Pinkus and C. D. Moon, unpublished work.

(38) Shortly after the time that the work was originally done,[1] nmr spectra were obtained on a Varian 30-MHz instrument; the authors express appreciation to N. F. Chamberlain, Humble Oil and Refining Co., Baytown, Texas, for these early spectra.