The percentages of the compounds were based on their adjusted areas in the chromatograms. The adjustments were based on the following determinations: the ratio of A_4/A_5 divided by W_4/W_5 is equal to 0.85; A_1/A_5 divided by W_1/W_5 is equal to 1.23; and A_3/A_5 divided by W_3/W_5 is equal to 1.18. The material balances were obtained by the internal-standard method using α-bromoethylbenzene. The area/weight ratio for α-bromoethylbenzene to **5** was found to be 1.30.

Identification of the Products Formed in the Bromination of Butadiene in Methanol.—The chromatogram of the product from the bromination of butadine in methanol showed four peaks. The second and fourth peaks were identified as **4** and **5**, respectively, on the basis of having retention times and ir spectra identical with those of the authentic isomers, which were synthesized according to the procedure of Hatch, *et al.*[7]

The first peak was assigned to 4-bromo-3-methoxy-1-butene (**1**) on the following basis. The bromination product was fractioned and the compound responsible for the first peak was isolated in pure form, bp 51–52° (30 mm), as indicated by vpc analysis. The compound gave the correct analysis for a bromomethoxybutene, C_5H_9BrO. *Anal.* Calcd for C_5H_9BrO: C, 36.39; H, 5.497; Br, 48.43. Found: C, 36.27; H, 5.57; Br, 48.69. The infrared spectrum[8] indicated either **1** or **2**, since it contained the hydrogen absorption band for the CH_3O group at 2810 cm^{-1} and the terminal vinyl absorption band at 928 and 985 cm^{-1}. The nmr spectrum was complex, but supported the structure of **1** or **2** by showing relative areas of three vinyl hydrogens to six methyl, methylene, and methine hydrogens. The compound was assigned the structure of 4-bromo-3-methoxy-1-butene (**1**) rather than 3-bromo-4-methoxy-1-butene (**2**) on the basis of stability. Heating the compound for 45 min at 115° gave no detectable rearrangement to *trans*-1-bromo-4-methoxy-2-butene (**3**), which would definitely be expected[9] if the compound were **2**.

trans-1-Bromo-4-methoxy-1-butene (**3**) was synthesized unambiguously, and when analyzed by vpc was found to have a retention time identical with that of the third peak. The synthesis of **3** is outlined in the following sequence.

trans-1,4-dibromo-2-butene $\xrightarrow[\text{HOAc}]{\text{KOAc}}$

trans-2-butene 1,4-diacetate $\xrightarrow{\text{Ba(OH)}_2}$ bp 73–75° (0.30 mm)

trans-2-butene 1,4-diol $\xrightarrow{(CH_3O)_2SO_2}$ bp 92–97° (0.25 mm)

trans-4-methoxy-2-buten-1-ol $\xrightarrow{PBr_3}$ bp 76–79° (3.3 mm)

trans-1-bromo-4-methoxy-2-butene bp 51° (4.1 mm)

The infrared spectrum of each of the intermediates in the above synthetic sequence supported the proposed structure. The infrared spectrum of the synthesized **3** showed the following absorption bands:[7] 2810 (hydrogens of the CH_3O group), 965 (*trans* vinyl hydrogens, strong), and 572 and 595 cm^{-1} (CBr group). The molecular analysis corresponded to C_5H_9BrO. *Anal.* Calcd for C_5H_9BrO: C, 36.39; H, 5.497; Br, 48.43. Found: C, 36.43; H, 5.63; Br, 48.19.

(7) L. F. Hatch, P. D. Gardner, and R. E. Gilbert, *J. Amer. Chem. Soc.*, **81**, 5943 (1956).

(8) For a discussion of the position of absorption bands in the infrared, see D. Williams and I. Fleming, "Spectroscopic Methods in Organic Chemistry," McGraw-Hill Publishing Co. Ltd., London, 1966.

(9) For a general discussion of the greater thermodynamic stability of 1,4- compared with 1,2-addition products from the chlorination and bromination of butadiene and isoprene, see B. T. Brooks, "The Chemistry of the Nonbenzenoid Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1950, p 362–366. In support of our assignment of structure **1** to this compound rather than **2** on the basis of stability, we would like to indicate that, under identical conditions, **4** rearranges to **5**. Also, under nearly identical conditions, 3,4-dibromo-2-methyl-1-butene rearranges extensively. [See V. L. Heasley, C. L. Frye, R. T. Gore, Jr., and P. S. Wilday, *J. Org. Chem.*, **33**, 2342 (1968).] We also observed that, upon standing, *cis*-1-bromo-4-methoxy-2-butene slowly rearranges to *trans*-1-bromo-4-methoxy-2-butene (**3**). Only a trace of what may be 3-bromo-4-methoxy-1-butene (**2**) was detected. This definitely confirms the greater thermodynamic stability of **3** compared with **2**.

Registry No.—Butadiene, 106-99-0; *trans*-2-butene 1,4-diacetate, 1576-98-3; *trans*-2-butene-1,4-diol, 821-11-4; *trans*-4-methoxy-2-buten-1-ol, 22427-04-9; **1**, 22427-00-5; **3**, 22427-01-6.

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Conformation of Bicyclo[3.3.1]nonane Systems. A Semiempirical Investigation

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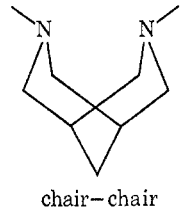
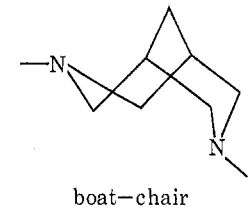
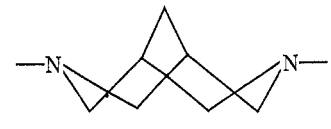
The structures of compounds belonging to the ring system bicyclo[3.3.1]nonane have been the subject of considerable interest in recent years.[1–6] Apart from various distorted structures, these species may exist in any of the following three conformations, all of which are free from bond-angle strain. In most of the cases studied thus far, the chair–chair structure with various degrees of distortion seem to be favored. Thus Brown,



chair–chair

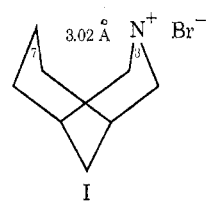


boat–chair

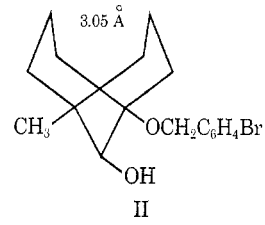


boat–boat

et al.,[2] and Dobler, *et al.*,[3] by their X-ray crystallographic studies, proved the chair–chair structures for compounds I and II with C_3–C_7 and N_3–C_7 distances of 3.05 and 3.02 Å, respectively. Douglass and Ratliff[1]



I



II

synthesized N,N′-dimethylbispidine and, based on dipole moment and nmr studies, tentatively assigned a flattened chair–chair structure for this compound.

(1) J. E. Douglass and T. B. Ratliff, *J. Org. Chem.*, **33**, 355 (1968).

(2) W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1844 (1965).

(3) M. Dobler and J. D. Dunitz, *Helv. Chim. Acta.*, **47**, 695 (1964).

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(5) H. S. Aaron, C. P. Ferguson, and C. P. Rader, *J. Amer. Chem. Soc.*, **89**, 1431 (1967).

(6) N. W. J. Pumphrey and M. J. T. Robinson, *Chem. Ind.* (London), 1903 (1963).

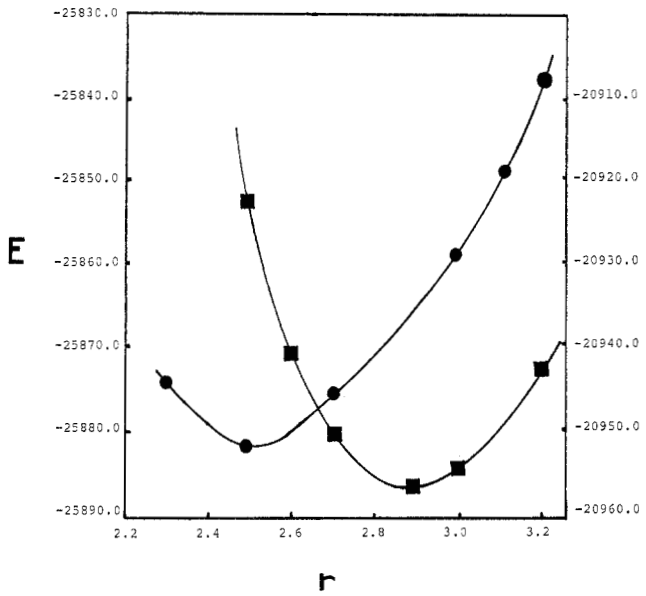

Figure 1.—Total energy calculated by the EHT method as a function of the distance between atoms in positions 3 and 7: ■, 3-azabicyclo[3.3.1]nonane; ●, N,N′-dimethylbispidine.

Unfortunately, however, the measured dipole moment does not unequivocally rule out the possibility of the chair–boat structure for this compound. We, therefore, carried out LCAO–MO calculations in order to throw some light on the structure of this compound.

Methods of Calculations. Extended Hückel MO Method.—The method is that developed by Hoffmann.[7] Calculations were made on an IBM 7040 computer using QCPE Program No. 30. Values of valence-state ionization potentials used in this calculation have been reported in the literature.[8,9]

CNDO/2 Method.—This method, developed by Pople and Segal,[10] is an LCAO–SCF method. Calculations were made on an IBM 7040 computer using QCPE Program No. 91, the output of which consists of total energy, charge densities, dipole moments calculated from charge densities, and dipole moments calculated from the effective charge densities taking into account the symmetries of the individual orbitals.

The C–C and C–H distances were assumed to be the same as those in cyclohexane and C–N distances were considered to be the same as C–C distances.

Results and Discussion

Hoffmann[7] used the extended Hückel method for obtaining the most probable conformation in several hydrocarbons. Here we applied this method for the bicyclo[3.3.1]nonane system. X-Ray data are available for compounds I and II. Of these two compounds, I has a nitrogen atom in position 3. We, therefore, decided to carry out calculations on this compound for its chair–chair conformation with various degrees of distortion. The energy values of this molecule and N,N′-dimethylbispidine for their chair–chair conformation were calculated in which the distance r between atoms in positions 3 and 7 was varied. The results are given in Figure 1. It is clear from this figure that the minimum energy value for compound I is obtained at an r value of 2.9 Å.

On the other hand, for N,N′-dimethylbispidine the minimum energy was obtained at an r value of 2.5 Å, which is the N–N distance in a normal chair–chair form. The main difference between N,N′-dimethylbispidine and compound I is the absence of *endo* hydrogen atoms in the former. It is, therefore, reasonable to expect less strain in the normal form of this compound than in the latter. Similar calculations on the chair–boat and boat–boat forms yielded higher energy values (Table I).

TABLE I
TOTAL ORBITAL ENERGY DIFFERENCES AND CALCULATED DIPOLE MOMENTS FOR VARIOUS CONFORMATIONS OF N,N′-DIMETHYLBISPIDINE

	E, kcal		Dipole moment, D	
Conformation	EHT	CNDO/2	Calcd[a]	Found
Chair–chair	0	0	2.2	...
Chair–boat	20.6	18.0	1.7	2.0 ± 0.2
Boat–boat	45.4	24.9	3.56	...

[a] Calculated complete dipole moment by CNDO/2 method. From ref 1.

The CNDO/2 method gives reliable dipole-moment data and relative conformations at fixed input bond lengths.[11–13] For large molecules, the calculations, even in a high-speed digital computer, are prohibitively time consuming. Hence we decided to carry out calculations only on the normal chair–chair, chair–boat, and boat–boat structures. The energy values and dipole moments for these structures are given in Table I. These energy values, when compared with those calculated by the EHT method, show the same trend. Energy values obtained by the SCF method seem more reasonable. To the best of our knowledge, the difference in the energy values for this type of bicyclic system have not been reported.

Cyclohexane is known to exist entirely in the chair conformation at room temperature. The energy difference between the chair and the boat forms of this molecule is still a subject of controversy. Reported values[14,15] range from 1.31 to 10.6 kcal/mol. Yousif and Roberts[16] reported the activation energy of the inversion of 4,4-difluoropiperidine to be 13.9 kcal/mol in methanol solution. The energy differences between the various conformations given in Table I are of similar magnitude. The calculated dipole moment for the chair–chair form agree with the experimental value[1] within the limit of the experimental error. We, therefore, conclude that at room temperature this molecule does exist entirely in a normal or near normal chair–chair form.

Registry No.—N,N′-Dimethylbispidine, 14789-33-4.

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