BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 1676—1682 (1970)

Some Semi-Empirical SCF MO Calculations on Norbornadiene, Norbornene, and Their 7-Cations

Hideyuki Konishi, Hiroshi Kato[*1] and Teijiro Yonezawa

Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto

(Received December 13, 1969)

Using a semi-empirical SCF MO method for valence electron systems proposed previously by the present authors, the electronic structures of norbornadiene (NBD), norbornene (NBE), and their 7-cations are discussed, together with the configurational problem of the 7-cations. In NBE and NBD, the interaction between the π AO's in the double bond and the AO's of the other parts of the molecules is made clear by the charge densities and the bond orders. For the first electronic transition assigned to a π–σ^* or σ–π^* in NBD, the present calcuation gives a rather larger excitation energy than does the experiment. For 7-norbornenyl and 7-norbornadienyl cations, the presence of structures distorted from NBE and NBD respectively can theoretically be concluded. The delocalization of the positive charge and the bonding interaction between the bridged carbon atom and the double bond carbon atoms support the concept of the so-called non-classical carbonium ions.

Norbornadiene (NBD), norbornene (NBE), and related compounds have been investigated from many points of view, such as reaction mechanisms,[1] electronic transitions,[2,3] and other physicochemical properties.[1] The first electronic band of NBD, which was identified as a forbidden π–π^* one,[4–6] has recently been pointed out to be a π–σ^* or σ–π^* one by Robin and Kuebler.[3] It seems interesting to include σ electrons in our theoretical studies in order to compare the electronic structures of NBD with earlier π-electron calculations.[4–6] An investigation of the σ electronic structures of NBD as well as of the π electronic structures is an aim of the present calculations, made by the semi-empirical SCF MO method for valence electron systems previously presented by the present authors.[7]

The carbonium ions of NBD and NBE have been discussed as so called non-classical carbonium ions.[1] In our study of the 7-carbonium ions of NBD and NBE, we have focussed our attention on the following four points: the distortion of the valence angle and the alternation of the bond length with reference to the neutral molecules, the migration of charges, and the non-bonding interactions in these ions.

Method and Parameters

The present calculations were performed by means of our previously-reported semi-empirical SCF MO method, using the zero-differential overlap approximation except for the one-center exchange integrals.[7] All the core-resonance integrals are taken into account in estimating the non-bonding interactions of atoms as:

$$H_{rs} = -KS_{rs}(I_r+I_s)$$

where K is a constant which will be described in a later part of this section, where S_{rs} is the overlap integral between the rth and the sth atomic orbitals (AO's), and where I_r denotes the valence-state ionization potential of the rth AO. The other parts of the present method and the basic integral values are the same as in our previous paper.[7]

For the geometry of NBD, the gas-electron diffraction datum reported by Morino *et al.*[8] is adopted. (All the skeletal carbon atoms for the compounds treated in the present paper are numbered as is shown in Fig. 1.) For the 5- and 6-carbon skeletal structures of NBE, the datum of norbornane[8] is used, while for the residual part,

---

[*1] Present address: Department of General Education, Nagoya University, Nagoya.

1) P. D. Bartlett, "Nonclassical Ions," Benjamin, N. Y. (1965).

2) S. Stokes and L. W. Pickett, *J. Chem. Phys.*, **23**, 258 (1955).

3) M. B. Robin and N. A. Kuebler, *ibid.*, **44**, 2664 (1966).

4) C. F. Wilcox, Jr., S. Winstein and W. G. McMillan, *J. Amer. Chem. Soc.*, **82**, 5450 (1960).

5) R. B. Hermann, *J. Org. Chem.*, **27**, 441 (1962).

6) N. L. Allinger and M. A. Miller, *J. Amer. Chem. Soc.*, **86**, 2811 (1964).

7) T. Yonezawa, H. Konishi and H. Kato, This Bulletin, **42**, 933 (1969).

8) Y. Morino, K. Kuchitsu and A. Yokozeki, *ibid.*, **40**, 1522 (1967).

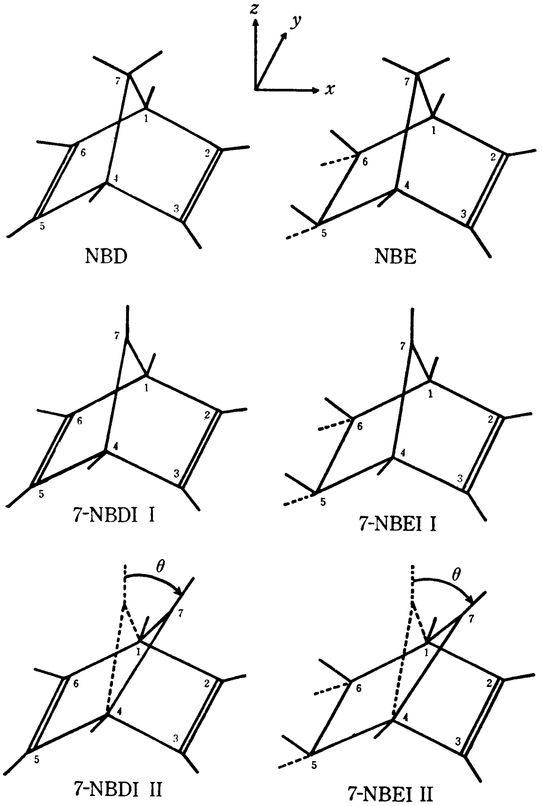

Fig. 1. Structures of NBD, NBE and their 7-cations.

that of NBD is adopted. In the 7-Norbornenyl and 7-norbornadienyl cations (7-NBEI and 7-NBDI), the sp^2 hybridization of the 7-carbon atoms is assumed, along with the same C–H bond distances as in the neutral molecules. The distortion of 7-NBEI and 7-NBDI is also investigated by moving the C_5, C_6, and C_7's, with their hydrogens, on arcs determined by fixing the plane formed by C_1, C_2, C_3, and C_4 carbon atoms and by keeping the C_s symmetry of the compounds and all the bond lengths unchanged. The distortion is indicated by the θ angle (illustrated in Fig. 1), which represents the displacement of the C_1, C_7, C_4-plane from its positions in the parent neutral molecule. The displacement of the C_1, C_4, C_5, C_6-plane is also tentatively taken to be $\theta/2$ in the same direction as the C_1, C_7, C_4-plane so as to reduce the strain on the compound.

The parameter, K, is taken to be 1.05, so that the calculated value of the lowest singlet transition energy of NBE may fit the observed value. The parameter dependence of several calculated quantities is presented in Table 1, together with the observed values. From this table, it may be noticed that the transition energies depend remarkably on the values of K, while the ionization potentials and the charge distributions are almost independent of the K values.

Table 1. Dependence of K values for the calculated quantities of NBE[a)]

K	1.00	1.05	1.10	obs.
I_p eV	9.84	9.87	9.91	9.05[b)]
V eV	6.13	6.35	6.56	6.33[c)]
Q_{C1}	+0.006	+0.004	+0.003	—
Q_{C2}	−0.124	−0.126	−0.128	—
Q_{C7}	−0.135	−0.136	−0.138	—

a) K, parameter in the equation of the core resonance integral; I_p, ionization potential; V, singlet $^1A' \rightarrow {}^1A''$ transition energy; Q_{CN}, net charge of the Nth carbon atom.

b) T. McAllister, Z. Dolešek, F.P. Lossing, R. Gleiter and P. R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 5982 (1967).

c) Ref. 11.

Results and Discussions

NBE and NBD. The charge distribution of NBE and NBD is recorded in Table 2. The π-charge densities on the unsaturated carbons are also shown, together with the other AO's.[10)] The calculated charge densities on the π AO's of NBE and NBD are larger than unity. This indicates the presence of electron delocalization due to interaction between the π AO's and the residual parts of the molecules. This can also be seen in the fact that the values of the π-bond orders, such as the $P_{\pi_2\pi_3}$ in both NBE and NBD, are less than unity.

The π AO coefficients[10)] of some of the MO's of NBE and NBD in Table 3 represent a measure of the localization of the MO's in the π AO's. For this purpose, the D quantity is defined as:

$$D(\text{NBE}) = 2\{C(\pi_2)\}^2$$

$$D(\text{7-NBEI}) = 2\{C(\pi_2)\}^2 + \{C(\pi_7)\}^2$$

$$D(\text{NBD}) = 4\{C(\pi_2)\}^2$$

$$D(\text{7-NBDI}) = 2\{C(\pi_2)\}^2 + 2\{C(\pi_5)\}^2 + \{C(\pi_7)\}^2$$

where $C(\pi)$ is the transformed π-AO coefficient of an MO. A large D value denotes the localization of electrons occupying the MO. The highest occupied (HO) MO's of NBE and NBD are least localized, as is indicated by the D values in Table 3.

The transition energies of NBE are presented in Table 4, together with the experimental values measured in an ultraviolet vacuum by Stokes and Pickett.[2)] The calculated values are obtained

---

[9)] R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964); *J. Amer. Chem. Soc.*, **86**, 1259 (1964).

[10)] The π-AO coefficients can be defined at every sp^2 carbon atom by transforming the MO coefficients to those of the p AO perpendicular to a local molecular plane. Therefore, in 7-NBDI the π AO's of the 2,5 and 7 carbon atoms are not parallel to one another.

TABLE 2. CHARGE DISTRIBUTION OF NBE, NBD AND THEIR 7-CATIONS

		NBE	7-NBEI		NBD	7-NBDI	
			I	II		I	II
C_1		3.996	4.002	3.992	4.002	4.006	4.000
C_2	πa)	1.029	1.005	0.936	1.032	1.004	0.960
	π'	0.987	0.953	0.970	0.977	0.948	0.954
	σ	1.039	1.045	1.054	1.037	1.044	1.050
	s	1.030	1.026	1.024	1.029	1.026	1.025
	total	4.085	4.028	3.984	4.075	4.024	3.989
C_5		4.126	4.110	4.126	4.075	4.024	4.046b)
C_7	π	—	0.278	0.430	—	0.243	0.346
	total	4.136	3.648	3.730	4.107	3.621	3.666
H_1		0.963	0.908	0.907	0.962	0.905	0.905
H_2		0.951	0.898	0.896	0.947	0.895	0.893
H_5		0.937 exo 0.935 endo	0.900 exo 0.889 endo	0.898 exo 0.894 endo	0.947	0.895	0.896
H_7		0.937 syn 0.942 anti	0.881	0.875	0.938	0.879	0.874
$P_{\pi 2 \pi 3}$		0.959	0.940	0.866	0.958	0.940	0.891
$P_{\pi 5 \pi 6}$		—	—	—	—	—	0.958
$P_{\pi 2 \pi 7}$		—	0.163	0.379	—	0.189	0.316

a) π, $2p_\pi$ AO; π', 2p AO which is orthogonal to π and σ AO's; σ, $2p$ AO directed to the double bond axis; s, $2s$ AO.

b) π, 1.019; π', 0.957; σ, 1.042; s, 1.028.

TABLE 3. AO COEFFICIENTS OF SOME MO'S OF NBE, NBD AND THEIR 7-CATIONS

		Symmetry	Orbital energy (eV)	C_2a)				C_7a)	D
				π	π'	σ	s	π	
NBE	LVb)	a″	2.27	0.6731	0.0047	−0.0028	−0.0004	—	0.91
	HO	a′	−9.87	0.5388	−0.0641	0.0101	0.0338	—	0.58
7-NBEI I	NLV	a″	−3.45	0.6535	0.0008	−0.0057	0.0064	—	0.85
	LV	a′	−7.00	0.1065	−0.1385	−0.0388	0.0844	−0.9255	0.88
	HO	a′	−15.77	0.5669	−0.0095	0.0328	0.0012	0.0596	0.65
NBD	NLV	a_2	2.52	0.4841	0.0842	−0.0545	−0.0456	—	0.94
	LV	b_2	1.74	0.4704	−0.0788	0.0457	0.0443	—	0.89
	HO	a_1	−9.87	0.3277	−0.1533	0.0709	0.0717	—	0.43
	NHO	b_1	−10.20	0.4727	0.1001	−0.0756	−0.0407	—	0.89
7-NBDI I	TV	a_2	−3.03	0.4831	0.0863	−0.0525	−0.0431	—	0.93
	NLV	b_2	−4.05	0.4522	−0.0809	0.0375	0.0476	—	0.82
	LV	b_1	−7.00	0.1075	−0.1197	0.0316	0.0738	−0.9286	0.91
	HO	a_1	−15.89	0.3000	−0.1566	0.1329	0.0631	—	0.36
	NHO	b_1	−15.91	0.4960	0.1196	−0.0722	−0.0517	0.0710	0.98

a) π, π', σ and s are the same AO's that are represented in Table 2.

b) LV, the lowest vacant; HO, the highest occupied; NLV, the next lowest vacant; NHO, the next highest occupied; TV, the third vacant from the occupied.

by taking account of the configuration interactions among a limited number of singly-excited configurations. The notation, f_π, is the oscillator strength contributed by all kinds of π AO's. The difference between f_{total} and f_π for the lowest transition of NBE can be attributed to the σ AO's participation.

All previous theoretical treatments of the electronic transition of NBD have been carried out for π-electrons.[4-6] In these treatments the first transition is forbidden, whereas the second one is

TABLE 4. CALCULATED TRANSITION ENERGIES (ΔE) OF NBE AND NBD

(a) NBE

State	Calcd[a]			Obsd[c]	
	ΔE_{ev}	f_{total}	f_{π}[b]	ΔE_{ev}	f
$^1A''$	6.29	0.270	0.239	6.33	0.15
$^1A''$	6.75	0.001	0.003	7.40	0.15
$^1A'$	6.36	0.031	0.008		
$^1A'$	8.18	0.020	0.006		

(b) NBD

State	Calcd[a]			Obsd[d]	
	ΔE_{ev}	f_{total}	f_{π}[b]	ΔE_{ev}	$\log \varepsilon$
$^1B_2$	5.92	0.133	0.126	6.70	~3.7
$^1B_2$	6.92	0.108	0.163		
$^1A_2$	5.83	0	0	—	
$^1B_1$	6.52	0.027	0.005	—	
$^1A_1$	6.93	0.002	0.001	5.95	~3.3
$^1A_1$	7.91	0.022	0.001	—	

a) The number of configurations in CI treatment are 13 for NBE and 22 for NBD.

b) oscillator strength contributed from π AO's.

c) Ref. 11.

d) Ref. 3.

allowed. Robin and Kuebler,[3] however, assigned the first transition to a $^1A_1 \rightarrow {}^1A_1$ species (corresponding to a π-σ^* or σ-π^* transition) on the basis of a vibrational analysis in the vapor phase.

The $^1A_1 \rightarrow {}^1A_1$ transition energy calculated by the present method (in Table 4 (b)) is considerably larger than the experimental energy. For the $^1A_1 \rightarrow {}^1B_2$ transition energy, the calculated value does not agree with the experimental finding. In view of these defects, there seems to be some room for improvements in the present theory.[11]

7-NBEI and -NBDI. The non-classical structures of the carbonium ions derived from NBE and NBD have been discussed previously.[1] The electron delocalization of the 5-norbornenyl cation by means of Hückel MO calculations was made by Simonetta and Winstein.[12] 7-NBEI was treated as a bishomocyclopropenyl cation by Woods, Carboni, and Roberts.[13] These treatments shows the stabilizing energies of the non-classical models due to electron delocalization, though they are estimated by means of Hückel MO calculations and empirical calculations of the strain energy. All the valence electrons of NBEI and NBDI were treated with an extended Hückel theory by Hoffmann,[9] who also discussed the charge distribution and the stable conformation of NBEI and NBDI. Recently, a more quantitative treatment for NBEI has been performed by Ohorodnyk and Santry using the CNDO method.[14]

The experimental evidence on 7-NBDI was obtained from the NMR spectra by Story *et al.*,[15] The signals for four kinds of protons in 7-NBDI show a structure with a C_s, not a C_{2v}, symmetry. Recently, the bridge flipping of 7-NBDI was detected also from the NMR spectra by Brookhart, Lustgarten, and Winstein.[16] Further, the existence of 7-NBEI was proposed by Winstein *et al.*[17] on the basis of the unusual reactivity and complete retention of configuration in the acetolysis of aniti-7-norbornenyl tosylate. In the present paper, the configuration and the electronic structures of 7-NBEI and 7-NBDI will be discussed.

To deal with a configurational problem, the total energy is obtained as a sum of the total electronic energy of the valence electrons and the repulsion energy between cores:

$$E_{\text{total}} = E_{\text{electronic}} + E_{\text{core}}$$

The E_{core} is approximated by a point-charge model as follows:[18]

$$E_{\text{core}} = \sum_{A<B}\sum Z_A Z_B e^2 / R_{AB}$$

where Z_A is the core charge of the atom A and where R_{AB} is the internuclear distance between the atoms A and B.

The calculated potential energy curves are plotted in Fig. 2 for 7-NBDI and 7-NBEI using the distortion described in the previous section. In 7-NBEI, the positive θ corresponds to the motion of the C_7 toward the double bond. The existence of the calculated potential minima at the angles different from zero for 7-NBDI and 7-NBEI in Fig. 2 supports

---

[11] In the present paper, the parameter, K, in the equation of the core-resonance integral is taken to be 1.05, whereas the value of 0.8 for benzene, pyridine, and so on (Ref. 7), and that of 0.9 for ethylene, have been adopted. The different values taken for K may suggest defects in the evaluation of the integrals, *e.g.*, the core-resonance integral and the Coulomb repulsion integrals.

[12] M. Simonetta and S. Winstein, *J. Amer. Chem. Soc.*, **76**, 18 (1954).

[13] W. G. Woods, R. A. Carboni and J. D. Roberts, *ibid.*, **78**, 5653 (1956).

[14] H. O. Ohorodnyk and D. P. Santry, *ibid.*, **91**, 4711 (1969).

[15] P. R. Story and M. Saunders, *ibid.*, **84**, 4876 (1962); P. R. Story, L. C. Synder, D. C. Douglass, E. W. Anderson and R. L. Kornegay, *ibid.*, **85**, 3630 (1963).

[16] M. Brookhart, R. K. Lustgarten and S. Winstein, *ibid.*, **89**, 6352 (1967).

[17] S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *ibid.*, **77**, 4183 (1955).

[18] If the total energy difference between a neutral molecule and its dehydrated cation (or between a neutral molecule and its protonated cation) is calculated on the basis of the point-charge model, the ionization energy (or proton affinity) becomes too small. In the present paper, where the E_{core} is used mainly in the distortion problem, this approximation can be used.

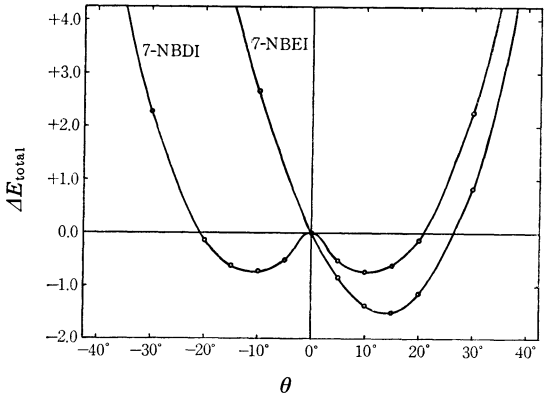

Fig. 2. Potential energy curves for distortion of the bridge in 7-NBEI and 7-NBDI.

the idea of non-classical structures of them. These results are also supported by Hoffmann[9,19] and Ohorodnyk and Santry,[14] though the angles of the potential minima differ among these treatments. The conclusion of Story *et al.*[15] obtained by means of NMR is also substantiated. The calculated potential minimum for 7-NBDI is obtained at $\theta=10°$, with the stabilization energy of 0.75 eV referred to the energy at $\theta=0°$. The present value of the stabilization energy is close to the values estimated by Brookhart, Lustgarten, and Winstein[16] by means of NMR spectroscopy ($\geq$0.85 eV). The calculated energy minimum for 7-NBEI is found at $\theta=15°$. In order to discuss the electronic structures of these ions with variable θ angles, we will hereafter use the following abbreviations: 7-NBDI I ($\theta=0°$), 7-NBDI II ($\theta=10°$), 7-NBEI I ($\theta=0°$), and 7-NBEI II ($\theta=15°$).

The charge distribution of the cations is presented in Table 2. The remarkable migration of the positive charge in the molecule may be a characteristic of a non-classical structure. The positive charge on C_7 is not so large as those found by Hoffmann using the extended Hückel method.[9] In 7-NBEI II and 7-NBDI II, the $2p_\pi$ AO's of the C_2's lost a little charge compared with those in their neutral molecules, whereas the $2p_\pi$ AO's of the C_7's gained somewhat. This trend and the fairly large values of the $P_{\pi 2 \pi 7}$'s support our ideas as to the features of the nonclassical carbonium ion. (A more detailed discussion will be given below.)

In our previous paper,[7,20] we used a semiempirical relation between the bond length and the $E_{AB}{}^1$ value of the AB bond, which corresponds to the bond energy, in estimating unknown bond lengths. In the

TABLE 5. CHANGES OF THE VALUES OF E^1_{AB} AND E^2_{AB} FOR 7-NBEI AND 7-NBDI (eV unit)

Bond[a]	NBE		7-NBEI			
			I		II	
	E^1_{AB}	E^2_{AB}	ΔE^1_{AB}	ΔE^2_{AB}	ΔE^1_{AB}	ΔE^2_{AB}
2—3	−41.17	47.90	+0.61	−0.05	+2.02	−0.06
5—6	−24.66	34.86	+0.29	−0.03	+0.14	±0
1—2	−25.98	35.31	+0.65	−0.03	+0.97	−0.03
1—6	−24.53	34.74	+0.45	+0.01	−0.28	±0
1—7	−23.58	33.20	−1.43	±0	−0.88	−0.01
(2—7)	−0.07	12.22	−1.03	−0.11	−3.39	+2.57

Bond[a]	NBD		7-NBDI			
			I		II	
	E^1_{AB}	E^2_{AB}	ΔE^1_{AB}	ΔE^2_{AB}	ΔE^1_{AB}	ΔE^2_{AB}
2—3	−41.32	47.89	+0.49	−0.04	+1.48	−0.04
5—6					+0.12	−0.03
1—2	−25.73	35.29	+0.55	±0	+0.87	±0
1—6					+0.01	±0
1—7	−23.38	33.20	−1.43	±0	−1.18	±0
(2—6)	−0.30	10.67	−0.10	−0.03	+0.08	−0.76
(2—7)	−0.10	12.21	−0.80	−0.10	−2.45	+1.58
(5—7)					−0.05	−0.68

a) the pair in the parenthesis is non-bonding one.

---

[19] The extended Hückel theory, which is not recklessly applicable to charged compounds,[9] can probably be applied to the distortion problem in the present case because the main contribution is by the electronic terms rather than by the Coulombic terms, as will be discussed later in terms of E^1_{AB} and E^2_{AB}.

[20] In Ref. 7, the E_{AB} notation is adopted instead of E^1_{AB} in the present paper.

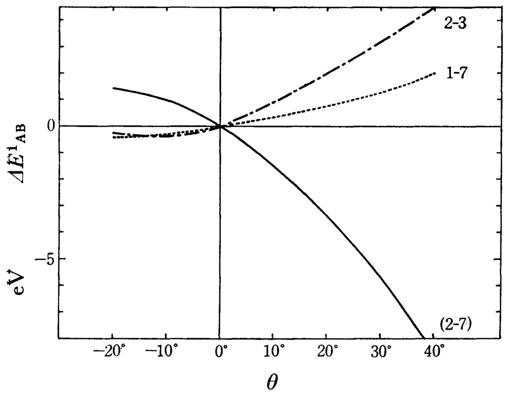

Fig. 3. Variation of E^1_{AB} values for 7-NBEI according to the distortion.

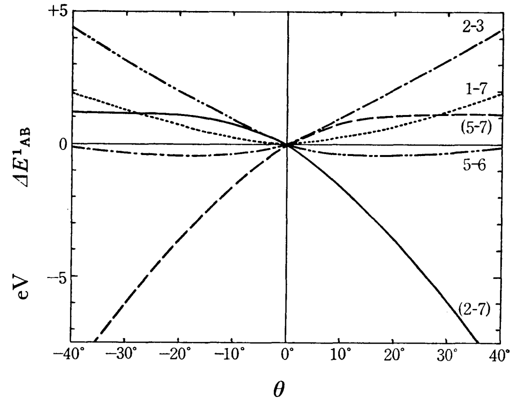

Fig. 4. Variation of E^1_{AB} values for 7-NBDI according to the distortion.

present paper, another index, $E_{AB}{}^2$, is introduced to discuss the strength of the heteropolan bond. The value of E_{AB}, which consists of $E_{AB}{}^1$ and $E_{AB}{}^2$ terms, can be used as a measure of the strength of a bond, where a stronger bond has a smaller value (see Appendix).[21]

In Table 5, the changes in the values of $E_{AB}{}^1$ and $E_{AB}{}^2$ for 7-NBEI and 7-NBDI, referred to NBE and NBD respectively, are tabulated. Based on these values for 7-NBEI I, which is assumed to have the same carbon skeleton as NBE, the trend of the alternation of the bond length can be confirmed. That is, all of the bonds in NBEI I, except for the 1–7 and 4–7 bonds, must be longer than those of NBE. Moreover, the non-bonding atomic distance between C_2 and C_7 (C_3 and C_7) can be predicted to become shorter than that of the neutral molecule. A similar trend can also be pointed out for 7-NBDI I. The $\Delta E_{AB}{}^1$'s of the non-bonding pairs of C_2 and C_7 for 7-NBEI II and 7-NBDI II have quite large absolute values, with a minus sign, though their $\Delta E_{AB}{}^2$'s also have large positive values. These facts indicate a partial bond characteristic of the so-called non-classical carbonium ions.

The variation in $E_{AB}{}^1$ values for 7-NBEI and 7-NBDI according to their distortion is illustrated in Figs. 3 and 4. For both cations, the interaction between C_2 and C_7 becomes stronger as θ increases, whereas the double bond (2–3) becomes weaker. The course of yielding the tricyclo-isomers[22] through

TABLE 6. CALCULATED TRANSITION ENERGIES (ΔE) OF 7-NBEI AND 7-NBDI

(a) 7-NBEI

I				II			
State	ΔE	f_{total}	f_π	State	ΔE	f_{total}	f_π
$^1A''$	2.98	0.004	0.000	$^1A''$	3.50	0.175	0.003
$^1A''$	3.93	0.002	0.001	$^1A''$	4.89	0.000	0.003
$^1A''$	4.58	0.007	0.001	$^1A''$	5.40	0.000	0.001
$^1A''$	6.47	0.262	0.227	$^1A''$	6.44	0.069	0.042
$^1A'$	2.92	0.043	0.018	$^1A'$	4.16	0.130	0.055
$^1A'$	4.23	0.003	0.010	$^1A'$	4.87	0.013	0.002
$^1A'$	5.42	0.013	0.006	$^1A'$	5.94	0.020	0.001

(b) 7-NBDI

I				II			
State	ΔE	f_{total}	f_π	State	ΔE	f_{total}	f_π
$^1B_2$	4.08	0.005	0.007	$^1A''$	4.10	0.003	0.004
$^1B_2$	5.99	0.083	0.033	$^1A''$	6.00	0.096	0.075
$^1A_2$	4.03	0	0	$^1A''$	4.50	0.001	0.006
$^1A_2$	5.61	0	0	$^1A''$	5.75	0.001	0.003
$^1B_1$	2.85	0.054	0.006	$^1A'$	2.98	0.053	0.017
$^1B_1$	4.66	0.006	0.006	$^1A'$	4.77	0.041	0.060
$^1A_1$	3.33	0.005	0.031	$^1A'$	4.02	0.009	0.002

---

[21] This point is connected with the relation between the values of E_{AB} and the experimental bonding energy attributed to the AB bond of a molecule (*cf.* a paper to be published).

[22] H. C. Brown and H. M. Bell, *J. Org. Chem.*, **27**, 1928 (1962); *J. Amer. Chem. Soc.*, **85**, 2324 (1963).

the carbonium ions can theoretically be expected, though there is a high potential barrier, accompanied by an alternation in the bond length and a variation in the valence angle.

The absorption spectra of these cations have been reported on only a little. The absorption band at 350 mμ (3.54 eV), which is assigned to an electronic transition in 7-NBDI by Winstein and Ordronneau,[23] is not compatible with the finding of Stofy and Saunders,[15] who found no absorption sbove 330 mμ (3.76 eV). The transition energies characteristic of the carbonium ions[24] are calculated to be slightly less than 3 eV for 7-NBDI (2.85 eV for I and 2.98 eV for II): these and the other results are presented in Table 6. Since we lack experimental data comparable with the present results, further experiments on the present problem must be undertaken.

In conclusion, the distorted configurations of 7-NBEI and 7-NBDI have been theoretically indicated. The delocalization of the positive charge and the bonding interaction between the bridged carbon atom and the double-bond carbon atoms, measured with $E^1_{\rm AB}$ and $E^2_{\rm AB}$ values, have been pointed out as the features of the so-called non-classical carbonium ions.

The calculations were carried out at the computation centers of both Tokyo University (HITAC 5020E) and Kyoto University (HITAC 5020).

Appendix

The total electronic energy of the valence electrons is:

$$E_{\rm electoronic} = \frac{1}{2}\sum_r \sum_s P_{rs}\,(H_{rs}+F_{rs}) \qquad \text{(A-1)}$$

where $\sum_r$ denotes the summation of all the valence AO's considered, and where P_{rs}, H_{rs}, and F_{rs} are, respectively, the bond order, the core-resonance integral, and Fock's operator between the rth and sth AO's. With the choice of a point-charge model for the repulsion energy between cores, the total energy of the molecule can be represented as follows:

where I_r is the valence-state ionization potential of the

$$E_{\rm total} = \frac{1}{2}\sum_r\sum_s P_{rs}\,(H_{rs}+F_{rs}) + \sum\sum_{\rm A<B} Z_{\rm A}Z_{\rm B}e^2/R_{\rm AB} \qquad \text{(A-2)}$$

The substitution of the one-center integrals presented in our previous paper[7] into Eq. (A-2) leads to the following expression:

$$\begin{aligned} E_{\rm total} &= \sum_{\rm A} E_{\rm A} + \sum\sum_{\rm A<B} E_{\rm AB} \\ &= \sum_{\rm A} E_{\rm A} + \sum\sum_{\rm A<B} (E^1_{\rm AB}+E^2_{\rm AB}) \qquad \text{(A-3)} \end{aligned}$$

Here, the monoatomic part, $E_{\rm A}$, and the diatomic parts, $E^1_{\rm AB}$ and $E^2_{\rm AB}$, are:

$$\begin{aligned} E_{\rm A} = &\sum_r^{\rm on\ A} P_{rr}\left[-I_r - \left(N_r - 1 - \frac{1}{4}P_{rr}\right)(rr/rr)\right] \\ &-\sum_{r}^{\rm on\ A}\sum_{<r}^{\rm on\ A}\left[P_{rr}(2N_{r'}-P_{r'r'})\left\{(rr|r'r') - \frac{1}{2}(rr'|rr')\right\}\right. \\ &\left.+\frac{1}{2}P^2_{rr'}\{(rr|r'r')-3(rr'|rr')\}\right] \qquad \text{(A-4)} \end{aligned}$$

$$E^1_{\rm AB} = \sum_r^{\rm on\ A}\ \sum_s^{\rm on\ B} P_{rs}\,(H_{rs}+F_{rs}) \qquad \text{(A-5)}$$

$$\begin{aligned} E^2_{\rm AB} = &\sum_r^{\rm on\ A}\ \sum_s^{\rm on\ B} (P_{rr}P_{ss}-P_{rr}N_s-P_{ss}N_r)(rr|ss) \\ &+ Z_{\rm A}Z_{\rm B}e^2/R_{\rm AB} \qquad \text{(A-6)} \end{aligned}$$

rth AO, where N_r is the number of valence electrons occupying the rth AO in the valence state, and where (rr/ss) and (rr'/rr') are the two-center Coulomb and one-center exchange repulsion integrals respectively. The relation between the $E_{\rm AB}$ and the experimental bonding energy attributed to the AB bond of a molecule is shown graphically. This will be presented in detail in a following paper. By the use of the positive hole approximation[25,26] instead of the point-charge model for the repulison energy between cores, $E^2_{\rm AB}$ can be expressed as follows:

$$E^2_{\rm AB} = \sum_r^{\rm on\ A}\ \sum_s^{\rm on\ B} (N_r-P_{rr})(N_s-P_{ss})(rr|ss) \qquad \text{(A-7)}$$

Thus, for two neutral atoms with P_{rr} equal to N_r, $E_{\rm AB}$ consists of only $E^1_{\rm AB}$. However for charged species, it should be necessary to take into account $E^2_{\rm AB}$ terms because of their large contributions, as is shown in Table 5.

---

[23] S. Winstein and C. Ordronneau, *ibid.*, **82**, 2084 (1960).

[24] For a carbonium ion, we generally noticed a small energy transition toward the lowest vacant MO, which lies very low.

[25] G. del Re and R. G. Parr, *Rev. Mod. Phys.*, **35**, 604 (1963).

[26] R. G. Parr and R. Pariser, *J. Chem. Phys.*, **23**, 711 (1955).