Electronic Structure of Lone Pairs. IV.[1] The Transannular Interaction of Several Meso-cycles

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The MO calculation of the transannular interaction of eight-membered model systems, containing S,O,N, or C atoms in the position opposed to the C atom of the C=O group, are made by the extended Hückel method and the semi-empirical ASMO SCF method. The relation between the bond order (P_{rs} value or E_{AB} value) and the infrared absorption frequency, $\nu_{C=O}$, is discussed. The electronic absorption maxima in the 221 mμ—235 mμ region are assigned to π-π^* type transitions of intramolecular charge transfer from the interacting atom, X, to the C=O group. The absorptions in the region from 217 mμ to about 190 mμ are n-σ^* type transitions. In the model calculation of the NH_3 and HCHO system, it is shown that the interaction is large, the lone pair being directed to the C atom.

The transannular interaction of diametrically-opposed nitrogen and carbonyl groups in meso-cycles was noticed formerly by Kermack and Robinson[3] in their work on alkaloid. Cromwell *et al.* reported[4] that the presence of an amino group (either substituted or unsubstituted) on the beta carbon atom of an α,β-unsaturated ketone lowers the carbonyl-streching band by 20—80 cm^{-1}. Many subsequent investigations have been performed by Leonard *et al.*[5–8] for the transannular nitrogen-carbonyl interaction in cyclic aminoketones and amino-acyloines of a medium ring size, such as compounds I,[5,6] II,[5,6] and III[5,9] in Fig. 1. They have shown that the occurrence of transannular interaction, $\mathrm{R{-}\overset{|}{N}^{\delta+}\colon\ \overset{|}{\underset{|}{C}}{=}O^{\delta-}}$, depends upon the ring size,[6,8,9] the strain,[7,9] and the environmental factors.[5,10] Further, they also established the transannular effects between sulfur or sulfoxide and ketone functions in an eight-membered model systems[11,12] (as IV[5,11] in Fig. 1). Namely, the lone pairs of nitrogen or sulfur atom have a through-space interaction with the carbon atom of the >C=O group (denoted by C_{CO}), which is polarized as $>^{+\delta}C{=}O^{-\delta}$. The frequencies of the infrared absorption maxima of the C=O stretching, $\nu_{C=O}$, of the compounds (such as I, II, III, and IV in Fig. 1) are abnormally lower than those of the corresponding alkanones[5,11,12] (as V, VI, and VII in Fig. 1). This is probably due to a transannular interaction and may reflect the different bond orders, P_{CO}, of the C=O group in the various compounds in Fig. 1. Note that VII does not show a transannular interaction, in spite of the existence of the lone pair of the oxygen atom.

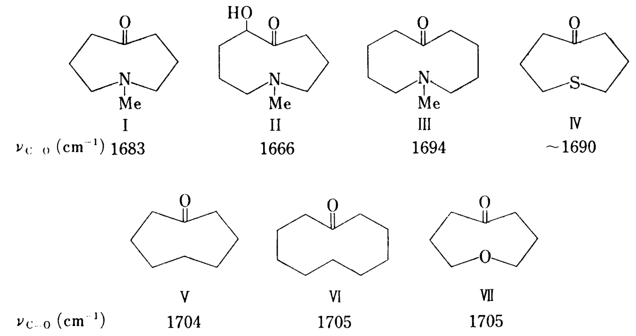

Fig. 1.

The UV spectra of these compounds observed by Leonard *et al.*[13] are reproduced in Tables 1A and 1B. In Table 1A, the maxima appear in the ~217 mμ region and ~264 mμ region for the compounds in which no appreciable transannular interaction is expected. On the other hand, the absorption maxima of the molecules in which the transannular interaction is expected appear in the region from 225 mμ to 231 mμ.[14] Similar relations[15] may be seen for the compounds listed in Table 1B. However, the assignments of these transitions have not yet been made.

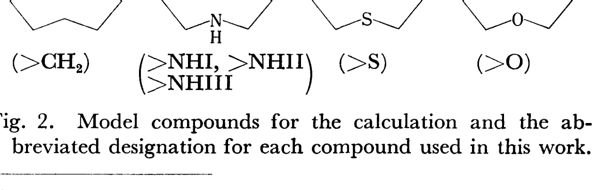

Fig. 2. Model compounds for the calculation and the abbreviated designation for each compound used in this work.

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[3] W. O. Kermack and R. Robinson, *J. Chem. Soc.*, **121**, 427 (1922).

[4] N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank, and D. J. Wallace, *J. Amer. Chem. Soc.*, **71**, 3337 (1949).

[5] N. J. Leonard and M. Ōki, *Kagaku no Ryoiki*, **10**, 1003 (1956) (in Japanese); K. Mutai, *ibid.*, **21**, 284 (1967); N. J. Leonard, *Rec. Chem. Prog.*, **17**, 243 (1956).

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[8] N. J. Leonard, R. C. Fox, and M. Ōki, *ibid.*, **76**, 5708 (1954).

[9] N. J. Leonard, M. Ōki, and S. Chivarell, *ibid.*, **77**, 6234, 6237 (1955).

[10] N. J. Leonard and M. Ōki, *ibid.*, **77**, 241, 6245 (1955).

[11] N. J. Leonard, T. W. Milligan, and T. L. Brown, *ibid.*, **82**, 4075 (1960); N. J. Leonard and C. R. Johnson, *ibid.*, **84**, 3701 (1962).

[12] Hs. H. Günthard and Th. Bürer, *Helv. Chim. Acta*, **39**, 356 (1956).

[13] N. J. Leonard and M. Ōki, *ibid.*, **77**, 6329 (1955).

[14] Leonard *et al.* describe how the bands at longer and shorter wavelengths observed for compounds 1 and 6 of Table 1A have disappear or are submerged under the strong 228 mμ band. For compounds 2, 3, 4, and 5, as the interaction between nitrogen and carbonyl is diminished, the intensity of the absorption in the 228 mμ region is decreased and the 217 mμ band becomes evident (Ref. 13).

[15] A "red shift" of the maximum at 227 mμ of >S for the polar solvent has been reported (Ref. 11).

TABLE 1A. ULTRAVIOLET ABSORPTION MAXIMA IN DIETHYL ETHER (REF. 13)

	Compound	λ, mμ	$\log \varepsilon$	λ, mμ	$\log \varepsilon$	λ, mμ	$\log \varepsilon$
1	2-Hydroxycyclononanone	217	2.65			264	2.13
II	1-Methyl-1-azacyclononan-5-ol-6-one	*		228	3.77	d	
2	1-Ethyl-1-azacyclononan-5-ol-6-one	*		226	3.62	d	
3	1-Isobutyl-1-azacyclononan-5-ol-6-one	217	3.49			d	
4	1-Isopropyl-1-azacyclononan-5-ol-6-one	218	3.47	$\sim$230	3.45	d	
5	1-*t*-Butyl-1-azacyclononan-5-ol-6-one	217	3.43	$\sim$231	3.37	d	
6	1-Methyl-1-azacycloheptadecan-9-ol-10-one	216	3.51			$\sim$270	1.98
I	1-Methyl-1-azacyclooctan-5-one	*		225	3.80	d	
III	1-Methyl-1-azacyclodecan-6-one	*		221	3.75	d	

d: Weak absorption in this region, no apparent maximum.
*: *cf* Ref. 3.

TABLE 1B. ELECTRONIC ABSORPTION MAXIMA IN CYCLOHEXANE (REF. 11)

	Compound	λ, mμ	$\log \varepsilon$	λ, mμ	$\log \varepsilon$	λ, mμ	$\log \varepsilon$
8	1-Thiacyclooctan-5-one-1-oxide	199	3.38	235	2.78	$\sim$290	1.3
IV	1-Thiacyclooctan-5-one	192	3.52	227	3.46	288	1.25
9	Methyl 4-ketopentyl sulfoxide (open chain)	207, $\sim$215	3.46	—	—	275	1.3
10	Methyl 4-ketopentyl sulfide (open chain)	198, $\sim$210	3.4	—	—	278	1.3
V	Cyclooctanone	$<$185	$>$2.9	—	—	288	1.18
11	Dimethyl sulfoxide	203	3.4	—	—	—	—

Furthermore, there have been several reports about biochemical interactions; it has reported that a lone pair of a nitrogen or a sulfur atom has a kind of a catalytic action through these transannular interactions[16,17] The important factor in these interactions is a favorable mutual situation of the interacting lone pair and the C=O group, and the maintenance of its situation in time and space, which will be done by the surrounding atoms and groups.[16,17]

The purposes of the present study are three-fold: (i) to ascertain whether the transannular interaction of the molecules can also be seen in the molecular orbital calculation; (ii) to ascertain the role of the lone pair in this interaction, and (iii) to determine the assignment of the main absorption maxima. Fig. 2 shows the electronic structures of some model compounds[20,21] which we investigated in Fig. 2. As a first trial method, the extended Hückel method[22] (abbreviated as E–H) is employed, because the system to be examined is large. Next, in order to ascertain the results by means of E–H calculation and to study the electronic transitions, semi-empirical ASMO SCF calculations[23] (abbreviated as SCF) for the valence electron systems are carried out, neglecting the contribution of the *d* orbitals.

When the molecule has a situation in which the direction of the lone pair to the C_{CO} atom is a ppropriate and the distance between them is one at which their potential energy is about at its minimum, a large transannular interaction may be expected. To show the existence of these critical values, we will make a model calculation of the electronic structure of the NH_3 and HCHO system, varying the mutual angle and distance between the NH_3 molecule and the HCHO molecule. At the same time, the variation in the atomic population,[24] the bond order of the C=O bond, P_{CO}, and the bond order between the C atom and the N atom, P_{CN}, are also studied.

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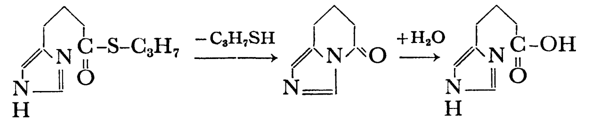
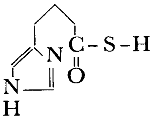
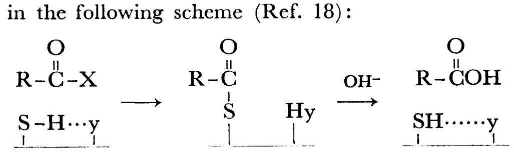
16) There is a report that, with the intramolecular assistance of the imidazole group, the following thiol-ester undergoes solvolysis at 10^6—10^7 times as fast as a normal thiol-ester. Its mechanism may be shown as follows (Refs. 18 and 19):



In our E–H calculation of a model compound,  the obtained bond order between the N atom and the opposed C_{CO} atom of the C=O group becomes positive and shows a transannular interaction.

17) An example of the transannular interaction, in the extended sense (through space interaction), is seen in the enzymatic action shown in the following scheme (Ref. 18):



18) "Organic Sulfur Compounds," ed. by N. Kharash, Pergamon Press (1961); Chap. 9 and 35, *etc.*, p 437 (Eq. (57)), p 438 (Eq. (58)).

19) T. C. Burice, *J. Amer. Chem. Soc.*, **81**, 5444 (1959).

20) The abbreviations, such as $>CH_2$, $>$NHI, $>$NHII, $>$S and $>$O, used for these compounds are shown in Fig. 2.

21) T. C. Bruice and B. Holmquist, *J. Amer. Chem. Soc* **89**, 4028 (1967).

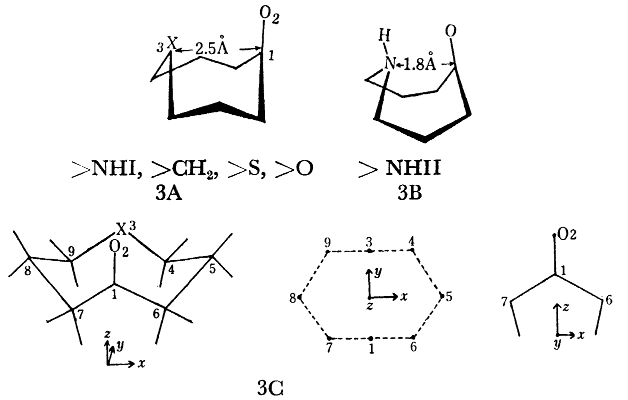
22) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); *ibid.*, **40**, 2745 (1964).

23) T. Yonezawa, H. Konishi, and H. Kato, This Bulletin, **42**, 933 (1969), Symposium of the electronic structure of molecules, Hokkaido, October, 1967.

24) K. Morokuma, H. Kato, T. Yonezawa, and K. Fukui, This Bulletin, **38**, 1263 (1965).

Method of Calculations

Figure 3 shows the conformations used for the MO calculations. The coordinate axes for the conformation of Fig. 3A[25] and the numbering of the atoms are given in Fig. 3C. As no definite conformation of these molecules has been reported, the calculation is carried out for the assumed structure, consulting the literature.[11] The bond lengths[26] and bond angles[26] employed are given in Table 2. With these lengths and angles, the $C_1 \cdots X_3$ distance (in Fig. 3A and Fig. 3C) becomes approximately 2.5Å. The y axis is chosen as the line connecting the interacting C_1 atom (C_{CO} atom) and the X_3 atom. The opposed triangle planes, $C_4X_3C_9$ and $C_6C_1C_7$, are parallel to each other, as in Fig. 3C. Namely, the dihedral angle, θ, between these two planes is set as zero.[27]



>NHI, >CH$_2$, >S, >O
3A

> NHII
3B

3C

Fig. 3. 3A and 3B show two conformations for the calculation. X denotes the N atom (of NH group), the C atom (of CH$_2$ group), the S atom or the O atom of each compound (Ref. 26. *cf* Fig. 2).
The coordinate axes for the conformation of 3A, and the numbering of the atoms are given in 3C.

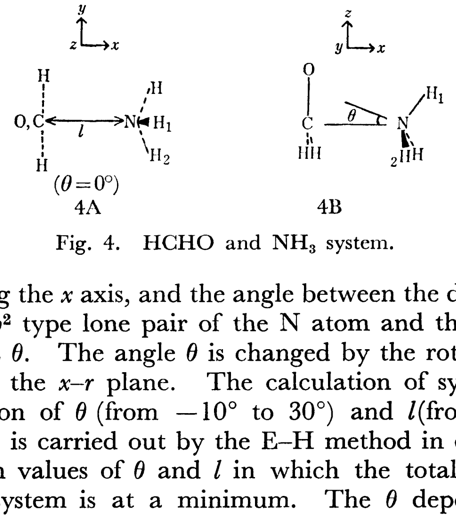
Table 2. Bond lengths (in Å) and bond angles

C–H	1.09	∠C (sp^2)	120°
C–C	1.54	∠C (sp^3)	109°28′
C=O	1.22	∠COC	112°
C–O (in C–O–C)	1.44	∠CSC	98°
C–S (in C–S–C)	1.82	∠CNC	107°
C–N (in C–N–C)	1.47		
N–H	1.01		

In this zero conformation the lone pair of the S atom will be approximately directed perpendicularly to the C=O bond.[28] However, the lone pair of the N atom is not directed in the way perpendicular to the C atom, but is directed slightly upwards. Then, for the compound containing the NH group, another limiting conformation, as in Fig. 3B, is calculated. This conformation is referered to as NHII, and the previous one, in Fig. 3A, as >NHI. In >NHII (Fig. 3B), the $C_1 \cdots N$ distance becomes shorter, 1.8 Å, and the derection of the lone pair of the N atom is more perpendicular to the plane including the C=O bond than in the case of >NHI.

Results and Discussion

Interaction of NH_3 and HCHO (A Model Calculation). In order to ascertain the interaction of the lone pair and the C=O group more explicitly, we calculated the electronic structure of the system of NH_3 and HCHO. HCHO is assumed to be planar, and the molecular plane is placed on the y–z plane, and the C=O bond, on the z axis, as in Fig. 4. The C···N distance is put as l along the x axis, and the angle between the direction of the sp^2 type lone pair of the N atom and the x axis is put as θ. The angle θ is changed by the rotation of NH_3 on the x–r plane. The calculation of system as a function of θ (from $-10°$ to $30°$) and l(from 0.5Å to 3.5Å) is carried out by the E–H method in order to ascertain values of θ and l in which the total energy of the system is at a minimum. The θ dependency of the atomic population[24] is shown in Table 3. The total energy and the bond order of the C–O bond, P_{CO}, and that between the C atom and N atom, P_{CN}, are shown in Table 4. The energy minimum is obtained at $\theta=0°$. The positive P_{CN} value indicates a bonding property between the C atom and the N atom. As θ approaches zero, the charge is transferred from NH_3 to HCHO, the polarization of the C–O bond and the P_{CN} value become large, and the P_{CO} value becomes smaller. Namely, the (transannular) interactions of the two molecules are the largest when the lone pair is directed to the C atom ($\theta=0°$).



4A 4B

Fig. 4. HCHO and NH_3 system.

As for the l dependency, the energy is decreased monotonically toward a larger l value and the expected energy minimum cannot be obtained by either method. This may be due to a defect in the approximation of the calculation.[29]

Population Analysis. The atomic orbital (AO) population[24] of the X_3 atom calculated by the E–H method and the AO-charge density[23] calculated by the SCF method are shown in Table 5. The AO population

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25) In Fig. 3A, X denotes the N atom of the NH group, the C atom of the CH$_2$ group, and the S atom or the O atom of the NHI, >NHII, >CH$_2$, >S, or >O compounds, respectively. In Fig. 3A, the H atom of the groups and CH$_2$NH are not shown, for the sake of simplicity.

26) "Tables of Interatomic Distances and Configuration in Molecules and Ions," ed. by L. E. Sutton, The Chem. Soc., London (1956) and (1965).

27) Leonard *et al.* estimated $\theta=21°$ for >0 and $\theta=68°$ for >S from the dipole moment (Ref. 11).

28) Actually, as the van der Waals radii of the sulfur atom are large, the molecule may have a larger dihedral angle than zero (Ref 27).

29) In the SCF calculation, the atomic-charge density and the E_{AB} values (E_{CO} and E_{CN}) do not change smoothly with the variation in θ and l.

TABLE 3. θ DEPENDENCY OF ATOMIC POPULATION OF HCHO AND NH_3

θ°	HCHO				NH_3			
	C	O	H	HCHO	N	H_1	H_2	NH_3
−10	3.0609	7.2154	0.8936	12.0635	6.1076	0.6100	0.6088	7.9364
0	3.0615	7.2156	0.8934	12.0640	6.1064	0.6098	0.6099	7.9360
5	3.0610	7.2155	0.8933	12.0631	6.1075	0.6096	0.6101	7.9368
10	3.0599	7.2153	0.8932	12.0616	6.1095	0.6093	0.6101	7.9383
20	3.0563	7.2145	0.8930	12.0568	6.1162	0.6086	0.6097	7.9432
30	3.0512	7.2133	0.8926	12.0498	6.1259	0.6077	0.6089	7.9501
40	3.0505	7.2131	0.8928	12.0493	6.1610	0.5994	0.5909	7.9506
*	3.0351	7.1755	0.8947	12.0000	6.1685	0.6105	0.6105	8.0000

* isolated molecule

TABLE 4. θ DEPENDENCY OF THE TOTAL ENERGY (IN eV) OF A HCHO AND NH_3 SYSTEM, AND BOND ORDER P_{CO} BETWEEN THE C ATOM AND THE O ATOM AND P_{CN} BETWEEN THE C ATOM AND THE N ATOM

θ°	−10	0	5	10	20	30	40
Total energy	−397.214	−397.220	−397.217	−397.210	−397.187	−397.151	−396.863
p_{C-O}	0.8252	0.8250	0.8251	0.8254	0.8262	0.8276	0.8277
$^{*}p_{C-N}$	0.0385	0.0394	0.0390	0.0380	0.0346	0.0296	0.0295

* bond order

TABLE 5. AO POPULATION (E–H) AND AO-CHARGE DENSITY (SCF) OF THE X ATOM

E–H

AO	atom				
	C (>CH_2)	N (>NHI)	S (>S)	O (>O)	N (>NHII)
s	1.198	1.512	1.531	1.782	1.484
x	0.949	1.281	1.072	1.424	1.269
y	1.154	1.717	1.806	1.976	1.248
z	1.035	1.485	1.586	1.852	1.375

SCF

AO	atom				
	C (>CH_2)	N (>NHI)	S (>S)	O (>O)	N (>NHII)
s	1.047	1.412	1.726	1.733	1.506
x	0.961	1.256	1.178	1.222	1.229
y	1.165	1.694	1.958	1.970	1.536
z	1.046	1.459	1.439	1.638	1.354

and the AO-charge density of the p_y AO of the N,S, and O atoms are large. These values of the p_y AO of the C atom are also larger than the p_x AO and the p_z AO. In the extreme case of >NHII, which is revealed to be too extreme, the electron of the p_y orbital flows to the p_y AO of the C_{CO} atom[30] and to the p_y AO of the O atom,[30] compared to the case of >NHI. This trend was also seen in the NH_3 and HCHO system, with a larger transannular interaction.

In the SCF calculation, according to a previous paper,[23] the total electronic energy, E_{AB},[23] of the AB bond is used instead of this bond order:

$$E_{AB} = \sum_{r}^{\text{on}A} \sum_{s}^{\text{on}B} P_{rs}(H_{rs}+F_{rs})$$

where H_{rs} is the core resonance integral,[23] where F_{rs} is the Fock's operator, and where $\sum_{r}^{\text{on}A}$ denotes the summation over all the valence AO's belonging to the A atom. The E_{AB} values obtained by the SCF calculation are listed in Table 6, together with the observed infrared absorption maximum of C=O stretching.[6,8]

TABLE 6. P_{rs} AND E_{AB} VALUES (eV) OF THE C=O BOND AND THE C_{CO}----X INTERACTION OBTAINED BY THE E–H AND THE SCF CALCULATIONS, AND THE OBSERVED CARBONYL FREQUENCY $\nu_{C=O}$(cm^{-1})

compound	E–H		SCF		
	P_{CO}	P_{CX}	E_{CO}	E_{CX}	$\nu_{C=O}$
>CH_2	0.791	0.015	−33.04	−0.36	~1704
>NH I	0.810	0.034	−34.03	−0.46	~1683
>S	0.755	0.149	−33.84	−1.19	~1690
>O	0.816	0.014	−34.04	−0.26	~1705
>NH II	0.455	0.361	−30.72	−7.62	—

The bond orders, P_{CX}'s, between the C_1 atom (or C_{CO} atom) and the X_3 atom (Fig. 3) become positive. This shows the bonding property (the transannular interaction) between the C_{CO} atom and the X atom. In Table 6, a correlation between P_{CO}, P_{CX}, E_{CX}, and $\nu_{C=O}$ may be expected. For the larger transannular interaction and the smaller $\nu_{C=O}$, the P_{CX} value becomes larger, the E_{CX} value becomes more negative, and the P_{CO} value becomes smaller. In the conformation with

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[30] The AO population of the p_yAO of the C_{CO} and O atoms of >NHI and >NHII are obtained as follows by the E–H calculations:

	>NH I	NH II
C_{CO}	0.405	0.649
O	1.789	1.931

TABLE 7. TRANSITION ENERGIES AND TRANSITION MOMENTS

	Transition	Type of transition	Transition energy			Transition moment M and its component			
			Calcd (eV)	Obsd (eV)	Obsd (mμ)	M	M(X)	M(Y)	M(Z)
$>CH_2$	$2 \rightarrow 1^*$	π-π^*	5.47	4.31	288 (a)	0.527	0.000	0.286	-0.443
	$1 \rightarrow 2^*$	n-σ^*	6.89	>6.70	<185 (a)	0.491	0.491	0.000	0.000
	$4 \rightarrow 1^*$	$n(\bar{\pi})$-π^*	6.72	—	—	0.100	0.000	0.034	0.094
$>NHI$	$2 \rightarrow 1^*$	π-π^*	6.30	5.51 (b)	225 (b)	0.374	0.000	-0.207	0.312
	$1 \rightarrow 3^*$	n-σ^*	6.89	— (c)	— (c)	0.515	0.515	0.000	0.000
	$4 \rightarrow 1^*$	$n(\bar{\pi})$-π^*	5.55	—	—	0.101	0.000	0.014	0.100
$>S$	$1 \rightarrow 1^*$	π-π^*	5.42	5.46	227 (e)	0.512	0.000	-0.386	0.336
	$2 \rightarrow 4^*$	n-σ^*	6.65	6.46	192	0.485	0.485	0.000	0.000
	$5 \rightarrow 1^*$	$n(\bar{\pi})$-π^*	6.53	—	—	0.202	0.000	-0.089	-0.181
$>O$ before CI	$3 \rightarrow 1^*$	$n(\bar{\pi})$-π^*	6.11	—	—	0.262	0.000	-0.107	0.239
	$2 \rightarrow 1^*$	π-π^*	6.47	—	—	0.238	0.000	-0.095	0.218
	$1 \rightarrow 3^*$	n-σ^*	6.73	—	—	0.583	0.583	0.000	0.000
after CI	$3 \rightarrow 1^*$	$n(\bar{\pi})$-π^*	6.08	—	—	0.191	0.000	-0.079	0.174
	$2 \rightarrow 1^*$	π-π^*	6.50	—	—	0.298	0.000	-0.120	0.273
	$1 \rightarrow 3^*$	n-σ^*	6.73	—	—	0.583	0.583	0.000	0.000

** : See Table 1A and 1B
(a): Ref. 11.
(b): These values are that of 1-methyl-1-azacyclooctane-5-one (Ref. 13).
(c): Probably the absorption in 217 mμ region will be masked (Ref. 1).
(e): Refs. 11, 2.

TABLE 8. ENERGY LEVELS CONCERNING THE TRANSITION OF TABLE 7 AND MAIN ORBITAL COEFFICIENTS OF THE C_1, O_2 AND X_3 ATOM

$>CH_2$

No of levels	$4(a')$	$2(a')$	$1(a'')$	$1^*(a')$	$2^*(a')$
Energy (eV)	-10.965	-9.757	-9.616	0.955	2.840
Type	$n(\bar{\pi})$	π	σ	π^*	σ^*
C_1	(Y) -0.094	(Y) 0.145	(X) -0.301	(Y) 0.788	(S) 0.602
	(Z) 0.181	(Z) 0.013		(Z) 0.012	
O_2	(Y) -0.149	(Y) 0.510	(X) 0.576	(Y) -0.489	(S) -0.082
	(Z) -0.277	(Z) -0.047		(Z) -0.006	
C_3	(Y) 0.070	(Y) 0.453	(X) -0.215	(Y) 0.079	(S) -0.050
	(Z) 0.366	(Z) -0.135		(Z) -0.061	

$>NHI$

No of levels	$4(a')$	$2(a')$	$1(a'')$	$1^*(a')$	$2^*(a')$
Energy (eV)	-10.962	-9.774	-9.323	1.468	3.270
Type	$n(\bar{\pi})$	π	σ	π^*	σ^*
C_1	(Y) -0.079	(Y) -0.084	(X) -0.297	(Y) 0.765	(S) 0.573
	(Z) 0.339	(Z) -0.031		(Z) 0.012	
O_2	(Y) -0.150	(Y) -0.332	(X) 0.680	(Y) -0.516	(S) -0.072
	(Z) -0.578	(Z) 0.061		(Z) -0.002	
N_3	(Y) 0.024	(Y) -0.621	(X) -0.104	(Y) 0.058	(S) 0.089
	(Z) 0.106	(Z) 0.282		(Z) -0.030	

$>S$

No of levels	$5(a')$	$2(a'')$	$1(a')$	$1^*(a')$	$3^*(a')$
Energy (eV)	-11.425	-9.574	-9.326	1.117	2.886
Type	$n(\bar{\pi})$	σ	π	π^*	σ
C_1	(Y) 0.125	(X) -0.274	(Y) -0.112	(Y) 0.715	(S) 0.542
	(Z) 0.250		(Z) -0.011	(Z) 0.035	
O_2	(Y) 0.230	(X) 0.710	(Y) -0.425	(Y) -0.481	(S) -0.054
	(Z) -0.436		(Z) 0.028	(Z) -0.016	
S_3	(Y) -0.241	(X) -0.117	(Y) -0.774	(Y) 0.105	(S) -0.015
	(Z) -0.519		(Z) 0.058	(Z) -0.148	

>O

No of levels Energy (eV) Type	$3(a')$ -10.095 $n(\bar{\pi})$	$2(a'')$ -9.937 π	$1(a'')$ -8.949 σ	$1^*(a')$ 1.551 π^*	$3^*(a')$ 3.310 σ^*
C_1	(Y) −0.095	(Y) −0.042	(X) −0.322	(Y) 0.789	(S) 0.615
	(Z) 0.189	(Z) −0.081		(Z) −0.006	
O_2	(Y) −0.288	(Y) −0.201	(X) 0.540	(Y) −0.523	(S) −0.085
	(Z) −0.257	(Z) 0.109		(Z) 0.007	
O_3	(Y) −0.160	(Y) −0.731	(X) −0.155	(Y) 0.054	(S) 0.040
	(Z) 0.284	(Z) −0.102		(Z) 0.009	

the dihedral angle larger than zero,[27,28] the P_{CX} value of >S becomes smaller and the parallelism with $\nu_{C=O}$ becomes better. When the NHII conformation is adopted (rather than >NHI), the parallelism becomes better. However, the total energy of >NHII is higher than>NHI, and the P_{CX}, E_{CX}, P_{CO}, and E_{CO} values of >NHII deviate too much[31] compared to the values of the other examples (see Table 6). That is, the>NHII conformation is too extreme. It is possible that an actual molecule may have an intermediate conformation[32] between the two, >NHI and >NHII (denoted hereafter by >NHIII), in which the total energy is at a minimum and the parallelism between the P_{rs}, E_{AB}, and $\nu_{C=O}$ values become better. However, since the two methods we employed cannot give an energy minimum for the variation in the distance between the C_{CO} atom and the X atom, it is difficult to determine the actual conformation of >NHIII in these approximations.

Electronic Transitions. The transition energy and the transition moment are calculated by the SCF method. The calculated results are listed in Table 7 and there compared with the observed UV absorpations. As for the π–π^* transition of the oxygen meso-cycles ($2\rightarrow1^*$ and $3\rightarrow1^*$ of Table 7) the configuration interaction (CI) is carried out. The results are shown in the bottom raws of Table 7. The energy levels concerning these transitions, and the main orbital coefficients of the C_1 or C_{CO}, O_2 and X_3 atoms, are shown in Table 8. The numbering of the levels is made from the highest-occupied level to the lower levels, and from the lowest unoccupied level (denoted by *) to the higher levels.

Though the agreement between the observed and the calculated transition energies is not very good, we tried to obtain some information about the nature of these transitions. The calculated transition with the higher energy is a sort of n–σ^* (A'') transition, the energy of which is equal for >CH_2 and >NHI, and does not vary very much for >S and >O. In the n MO, the MO coefficient of the lone pair AO of the O atom of the C=O group is large, and in the σ^* MO the MO coefficient of the s orbital of the C_1 atom is large. That is, it is noted that the n–σ^* transition is not affected very much by the transannular interaction. Therefore, these n–σ^* transitions correspond to the absorption is the 217 mμ region, which shows a comparatively small deviation among the compounds in Table 1A, or to the absorption about the 190 mμ region of the compounds in Table 1B.

The absorption maximum in the 230 mμ region (Tables 1A and 1B) may be a π–π^* (A')-type transition, in which π and π^* MO's are much more affected by the transannular interaction. That is, the π MO (see Table 8) is mainly constituted by the interacting lone pair AO and the π orbital of the C=O group. The π^* MO is considerably localized to the π^* antibonding orbital of the C=O group; the MO coefficient of the C_1 atom is especially large. Thus, these π–π^* transitions are essentially the intramolecular charge transfer from the interacting atom, X, to the C=O group.

In our calcultion, the transition with the third intense transition moment becomes an $n(\bar{\pi})$–π^* type (A'). The orbital, denoted by $n(\bar{\pi})$, has a comparatively large MO coefficient of the lone-pair AO of the O atom of the C=O group. In Table 7, the $n(\bar{\pi})$–π^* transition energy of NHI is smaller than the π–π^*. Possibly, the weak absorption with no detectable maximum in the longer-wavelength (carbonyl) region (shown by d in Table 1A)[13] is due to this $n(\bar{\pi})$–π^*-type transition.

From preceding calculations and discussions, it is found that the P_{CX} value is positive and the E_{CX} value is negative; this indicates the transannular interaction of the bonding type. Because of the larger transannular interaction, the P_{CO} value becomes large. The approximate parallelism between the P_{CO} value and $\nu_{C=O}$ is seen. Furthermore, the πMO, which is mainly constituted by the interacting lone-pair AO and the π orbital of the C=O group, and the π–π^* transition are affected by the transannular interaction.

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The calculation was carried out on a HITAC 5020 Computer at the computation center of the University of Tokyo.

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31) The P_{CO}, P_{CX}, E_{CO}, and E_{CX} values are sensitively change depending on the interatomic distance between the C_{CO} atom and the X atom.

32) The >NH III contormation has an intermediate $C_{CO}\cdot\cdot X$ distance between the two.