A Molecular Orbital Treatment of Triallyl Isocyanurates and Related Allyl Esters

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Triallyl cyanurate is known to be synthesized by the Schotten-Baumann reaction of allyl alcohol with cyanuric chloride[1,2]. Poly(triallyl cyanurate)[2] and triallyl cyanurate copolymer[2,3] with unsaturated polyester or other vinyl monomers have an excellent acid, alkali and heat-resistance. On the other hand, triallyl isocyanurate was prepared by the reaction of allyl chloride with potassium cyanate in acetonitrile[4] as the solvent under superatomospheric pressure, but it was not obtained in the pure crystalline form. Accordingly its melting point had not been known until triallyl isocyanurate was efficiently synthesized in our laboratory by a new method. It was carefully purified to polymerization[5]. Triallyl isocyanurate[5] which boils at 146°C/6 mmHg and melts at 23~25°C, polymerizes alone or copolymerizes with a number of vinyl monomers. The polymerization is catalyzed by peroxide to form a hard clear polymer[5].

As a preliminary consideration in connection with the experiments stated above, we are going to investigate theoretically their chemical reactivity, stability and other physical properties of some isocyanurates by the simple LCAO treatment.

The theoretically predicted properties have been found to agree well with those of the compounds which were synthesized, polymerized and treated with some reagents in our laboratory[6]. In the early stage of investigation of cyanurates and isocyanurates, Hantzsch and Bauer[7] reported the formation of mixed esters having alkyl groups on both the N and the O atom in one and the same triazine ring, and some additional, indirect evidences[8] were obtained which stood for the existence of *O,O,N*-ester (Drittel-pseudo-Cyanursäure-ester and *O,N,N*-ester (Zweidrittel-pseudo-Cyanursäure-ester). However subsequent attempts by Slotta and Tschesche[9] to prepare the mixed esters by methods diffenent from the above resulted in failure to lead them to the "Principle of Symmetry".

π-Electron Distribution in Cyanate Group.— Metal cyanates are hydrolyzed by water to liberate the active cyanate anion[10]. The isocyanate group of organic isocyanates is characterized by the polymerization or self-condensation and the condensation with various reagents containing active hydrogen atom[11]. Hence, in the first stage of LCAO molecular orbital investigation on the physical properties of isocyanurates, we calculate the π-electron distribution of NCO anion which is considered as a structural component of isocyanurates. The calculated values of total π-electron density, net charge and frontier electron density in each atom of NCO anion are listed in Table I.

TABLE I. THE ELECTRON DENSITY IN $(NCO)^-$ ANION

	N	C	O
Total π-electron density	1.7204	0.6507	1.6290
Net charge	−0.7204	+0.3493	−0.6290
Frontier electron density	1.4627	0.0315	0.5048

TABLE II. THE VALUES OF FRONTIER ELECTRON DENSITY AND ONE TERM APPROXIMATION OF SUPERDELOCALIZABILITY OF THE ACTIVE METHYLENE AND THE γ-CARBON IN ALLYL GROUP IN FOUR ESTERS

Ester	$f_{=H_2}$	$S'_{=H_2}$	$f_{=CH_2}$	$S'_{=CH_2}$
N,N,N-	0.0794	0.1145	0.1049	0.1513
N,N,O-	0.1581	0.2692	0.1089	0.1855
N,O,O-	0.1393	0.2306	0.1053	0.1743
O,O,O-	0.0847	0.1398	0.0646	0.1066

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[1] J. R. Dudley, J. T. Thurston, F. C. Schaefer, D. Holm-Hansen, C. J. Hull and P. Adams, *J. Am. Chem., Soc.*, **73**, 2986 (1951).

[2] H. M. Day and D. G. Patterson, *Modern Plastics*, **29**, July, 116 (1951).

[3] P. M. Elliott, ibid., **29**, July, 113 (1951); H. W. Starkweather, Jr., A. Adicoff and F. R. Eirich, *Ind. Eng. Chem.*, **47**, 302 (1955); W. Cummings and M. Botwick, ibid., **47**, 1317 (1955).

[4] D. W. Kaiser, U. S. Pat. 2536849 (1951).

[5] K. Fukui and H. Kitano, Japanese Pat. 7835 (1960).

[6] K. Fukui, H. Kitano and F. Tanimoto, unpublished work (1958).

[7] A. Hantzsch and H. Bauer, *Ber.*, **38**, 1005 (1905).

[8] A. Hantzch, *Z. anorg. Chem.*, **209**, 213 (1932).

[9] K. Slotta and R. Tschesche, *Ber.*, **60**, 301 (1927).

[10] O. Masson and I. Masson, *Z. physik. Chem.*, **70**, 290 (1910).

[11] R. G. Arnold, J. A. Nelson and J. J. Verbanc, *Chem. Revs.*, **57**, 47 (1957).

TABLE III. THE VALUES OF TOTAL π-ELECTRONIC ENERGIES AND CONJUGATION ENERGIES OF FOUR ESTERS

Ester	ε	$\varDelta E_\pi$
N,N,N-	$24\alpha+44.5572\beta$	$1.5293\ (-\beta)$
N,N,O-	$24\alpha+42.3475\beta$	$1.5451\ (-\beta)$
N,O,O-	$24\alpha+40.1390\beta$	$1.5620\ (-\beta)$
O,O,O-	$24\alpha+37.9162\beta$	$1.5647\ (-\beta)$

TABLE IV. THE VALUES OF PARAMETERS USED IN OUR CALCULATION

Coulomb integrals	Resonance integrals
$\alpha_{=\mathrm{H}_2}=\alpha-0.5\beta$	
$\alpha_\mathrm{N}=\alpha+\beta$	$\beta_{\mathrm{C}=\mathrm{H}_2}=2\beta$
$\alpha_{=\mathrm{O}}=\alpha+2\beta$	$\beta_{\mathrm{C}=\mathrm{O}}=\sqrt{2}\,\beta$
$\alpha_{-\mathrm{O}-}=\alpha+\beta$	$\beta_{\mathrm{C}-\mathrm{O}-}=\beta$
$\alpha_{\mathrm{O}^-}=\alpha+1.5\beta$	$\beta_{\mathrm{N}-\mathrm{C}}=\beta$

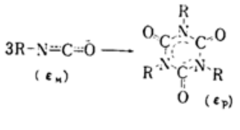
The results show that a polarization occurs through the transfer of an electron from the carbon atom to the nitrogen and the oxygen atoms in NCO anion. It is calculated that the nitrogen atom is the reaction position in its nucleophilic attack, referring to the values of reactivity indexes, in particular to the magnitude of the frontier electron density of this anion as a nucleophilic reagent. The values of parameters used in the calculation throughout the present paper are listed in Table IV.

The Stability of the Isocyanuric Ring. — To investigate the stability of the isocyanuric ring, we calculated the conjugation energy ($\varDelta E_\pi$) and the resonance energy (E_R) of isocyanuric acid triester. The results obtained are compared with values of benzene.

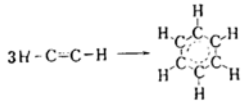
Conjugation Energy.—The conjugation energy ($\varDelta E_\pi$) is defined as follows:

$$\varDelta E_\pi=3\varepsilon_\mathrm{M}-\varepsilon_\mathrm{P}$$

where ε_P is the total π electron energy of an isocyanurate, and ε_M is that of the isocyanate. Since the group R is not a conjugative one, it is left out of account in the calculation. An isocyanurate ring consists of three isocyanate molecules as follows:



Then the conjugation energy, $\varDelta E_\pi$, defined above becomes 1.4888 $(-\beta)$, while with regard to benzene,



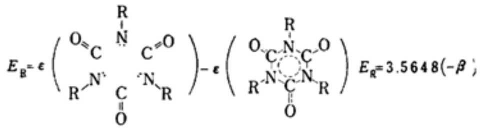
we obtain $\varDelta E_\pi=2(-\beta)$.

Resonance Energy.—The resonance energy E_R is defined

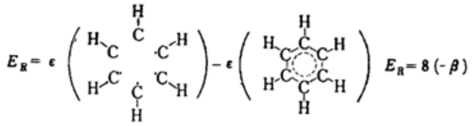
$$E_\mathrm{R}=\varepsilon_\mathrm{L}-\varepsilon_\mathrm{P}$$

where ε_L is the total π electronic energy of an extreme structure in which each two π electrons are localized in each bond.

Therefore, on an isocyanurate, the resonance energy is defined as



In a similar way, we calculate the resonance energy of benzene by the following equation.



Thus we know that the conjugation energy of an isocyanurate molecule is equal to ca. 75% of that of benzene, the resonance energy of the former being 44% of benzene.

These results will account for the remarkable heat stability of the isocyanuric ring[12].

The Stability and Reactivity of Triallyl Cyanurate and Isocyanurate. — Four structural isomers of triallyl ester are indicated as *O, O, O*-, *O, O, N*-, *O, N, N*- and *N, N, N*-esters. In these are included the isomeric esters of Hantzsch and Bauer[7]. Their structure and the electrophilic frontier electron densities (f_r) are indicated in Fig. 1. We calculate further the one term approximation of superdelocalizability (S'_r)[13], the total π-elecronic energy (ε), the conjugation energy $(\varDelta E_\pi)$*, and the energy of the highest occupied orbital (ε_f).

The calculated results enable us to derive the following conclusions.

Reactivity of Double Bond in Polymerization and Radical Reactivity.—The values of electrophilic frontier electron density (f_r) and one term approximation of superdelocalizability (S'_r) of the methylene radical in allyl group

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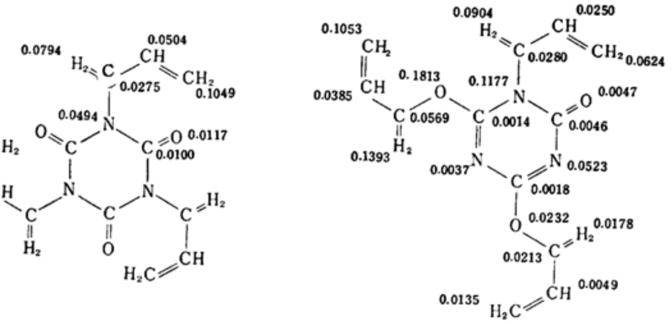
[12] P. Lemoult, *Ann. chim. phys.*, (7) **16**, 338 (1848); A. Hofmann, *Ber.*, **3**, 264 (1879).

* In the present calculation, allyl group is taken into consideration.

[13] K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **27**, 1247 (1957).

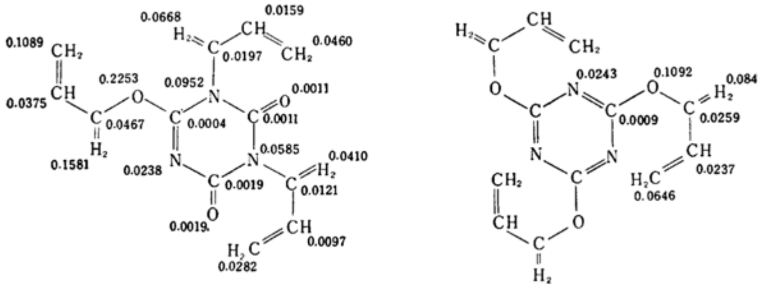
N, N, N-Ester *N, O, O*-Ester



$\varepsilon_f = \alpha + 0.6157\beta$
$\varepsilon = 24\alpha + 44.5572\beta$
$\Delta E_\pi = 1.5293(-\beta)$

$\varepsilon_f = \alpha + 0.6042\beta$
$\varepsilon = 24\alpha + 40.1390\beta$
$\Delta E_\pi = 1.5620(-\beta)$

N, N, O-Ester *O, O, O*-Ester



$\varepsilon_f = \alpha + 0.5872\beta$
$\varepsilon = 24\alpha + 42.3475\beta$
$\Delta E_\pi = 1.5451(-\beta)$

$\varepsilon_f = \alpha + 0.6600\beta$
$\varepsilon = 24\alpha + 37.9162\beta$
$\Delta E_\pi = 1.5647(-\beta)$

Fig. 1. Frontier electron densities, frontier orbital energy, total π-electronic energy and conjugation energy of four triallyl esters.

and the γ-carbon atom in allyl group of the isomeric esters are listed in Table II, in which are indicated the maximum values among three allyl groups of each monomer. It is found in the table that the reactivity of the methylene radical in allyl group decreases in the order *N, N, O*-; *N, O, O*- > *O, O, O*- > *N, N, N*-ester. It is worthy of note that the methylene radical in asymmetric esters should be more reactive than those in symmetric esters.

Pure triallyl isocyanurate was easily polymerized in the presence of benzoyl peroxide to give clear resin. The activation energies of the radical polymerization were observed 20.6 kcal./mol. for the *N, N, N*-ester and 43.2 kcal./mol. for the *O, O, O*-ester⁶⁾. Further, the order of electrophilic reactivity of double bond in isomeric esters is shown to be *N, N, O*-; *N, N, N*-; *N, O, O*- ≫ *O, O, O*-ester. This result is important, because it gives us a certain of information on the reactivities of these esters in cationic polymerization.

Reaction and Heat-stability of Triallyl-cyanurate and Isocyanurate.—The values of total π-electronic energy (ε) and conjugation energy (ΔE_π) of the isomeric esters are listed in Table III. As far as π-electronic energies in these esters are concerned, the values of ΔE_π seem to indicate that the ease of hydrolysis and transesterification of allyl groups decreases in the order *O, O, O*- > *N, O, O*- > *N, N, O*-> *N, N, N*-ester, if we consider the fact that a change in activation energy parallels closely to a change of ΔE_π. Furthermore, referring to the values of ε, esters formed may have a tendency to isomerize to the *N, N, N*-ester and through this isomerization these esters beome stabilized.

In our experiments⁶⁾, however, the *N, N, N*-ester could not be prepared from the *O, O, O*-ester by thermal isomerization, because the *O, O, O*-ester decomposes and polymerizes during distillation at atmospheric pressure. On the other hand, the *N, N, N*-ester could be distilled at 289°C/760mmHg in nitrogen current. Further, the infrared spectroscopic results⁶,¹⁴⁾ for the polymer of the *O, O, O*-ester showed

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14) B. H. Clampitt, D. German and J. R. Galli, *J. Polymer Sci.*, **27**, 515 (1958).

that a sort of *N, N, N*-ester structure had been formed by an isomerization during the polymerization process.

On the other hand, the weight loss on 1 hr. exposure to 300°C of the resin which was prepared by polymerization initiated by benzoyl peroxide was below 5% for the *N, N, N*-ester polymer and above 7% for the *O, O, O*-ester polymer⁽⁶⁾. These results indicate that the two polymers stated above are not completely identical and the *N, N, N*-ester polymer possesses a better heat stable property and a larger resistance for air oxidation than *O, O, O*-ester polymer.

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