MNDO Studies on Malononitrile Dimerization

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The reaction path of malononitrile dimerization, the intermediates and the tautomerism of the final product have been investigated by the MNDO method. The results are in good agreement with experimental data. The mechanism has a barrier height of about 88 kJ/mol and involves an intermediate which passes to the most stable tautomer through intermolecular proton transfer.

As a starting reagent in organic synthesis, malononitrile-dicyanomethylene has an established position because of its reactivity in the addition, self addition, and condensation reactions leading to various carbocyclic and heterocyclic systems [1]. The aim of our work is to investigate the reaction path of malononitrile dimerization and the structure of the reaction product using quantum mechanical methods.

It was shown that malononitrile undergoes a Thorpe-type dimerization in aqueous solution [2]: i) in the presence of bases [1], ii) in the autocatalytic formation at high pressure, 8000 kg/cm^2 at 323–343 K [3], iii) and under hydrogen pressure in the presence of the Pt catalyst with the apparent activation energy 85.8 kJ/mol [4] 1,1,3-tricyano-2-amino-1-propane is the main product in all cases. Bloch and Toupance [5] showed that the initial formation rate of the dimer in dilute aqueous solution is proportional to the square of the total malononitrile concentration and displays a maximum when the pH of the medium equals the pK_α of the following acid-base pair at a given temperature:

$$NC-CH_2-CN \rightleftarrows NC-\bar{C}H-CN + H^+ .$$

This behaviour can be interpreted by a reaction between one molecule of malononitrile and one molecule of the malononitrile anion.

Calculation

All calculations were carried out using the MNDO program/Modified Neglect of Differential Overlap, a semiempirical version of the Roothaan-Hall /RH/ SCF LCAO MO method in the NDDO approximation [6]. The molecules were assumed to be in their ground state. The calculations were performed on the CDC CYBER 72 computer in the Regional Computational Center "CYFRONET" at Kraków.

Ground State of Malononitrile and the Malononitrile Anion

Figure 1 shows the geometry of malononitrile calculated by the MNDO method with full geometry optimization for C_{2v} symmetry. The results agree well with the experimental data obtained by microwave [7] and crystallographic techniques at 235 K [8]. Similarly, good agreement has been achieved between the nine lowest experimental [9] and calculated ionization potentials assuming Koopman's theorem (Table 1) [10]. Larger differences were observed only in the orbital energies which correspond to the lone pairs of the nitrogen atoms. The MNDO method overestimates a lone pair orbital energy by 1.0 ÷ 1.1 eV [11]. The correction of these calculated values by 1.1 eV gives values very close to the

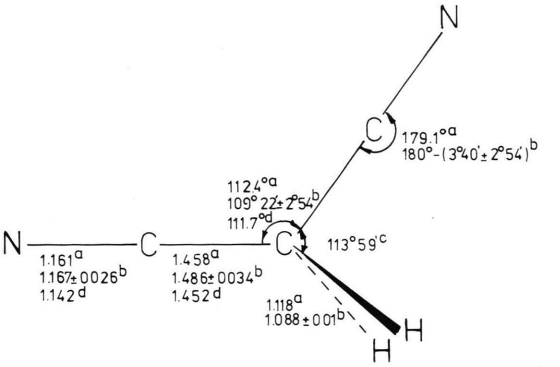

Fig. 1. Calculated and experimental geometry of malononitrile. Bond length in Å. a) MNDO results, b) Ref. 7a, c) Ref. 7b, d) Ref. 7c.

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Table 1. The nine lowest measured ionization potentials of malononitrile [9], calculated by MNDO, calculated by the X_α method [12], and assignments of the orbitals.

I.P. (eV)	1	2	3	4	5	6	7	8	9
Exp.	12.68 $b_1(\pi_{CN})$	13.20 $b_1(\pi_{CN})$	13.41 $a_1(n_N)$	13.59 $b_2(n_N)$	13.89 $a_1(\pi_{CN})$	14.02 $a_1(\pi_{CN})$	17.28 $a_1(\delta_{CH})$	18.10 $b_1(\delta_{CN})$	19.10 $b_2(\delta)$
MNDO	12.99 $b_1(\pi_{CN})$	13.49 $a_1(\pi_{CN})$	13.51 $b_1(\pi_{CN})$	13.60 $a_1(n_N)$	13.84 $a_1(\pi_{CN})$	14.04 $b_2(n_N)$	16.60 $b_1(\delta_{CH})$	18.28 $a_1(\delta)$	20.79 $b_1(\delta_{CC})$
X_α	13.74 $b_1(\pi_{CN})$	14.30 $b_2(\pi_{CN})$	14.37 $a_1(\pi_{CN})$	14.45 $a_2(\pi_{CN})$	16.25 $b_2(\pi_{CN})$	16.96 $a_1(n_N)$	16.98 $b_2(n_N)$	17.50 $a_2(\delta_{CH})$	19.38 $b_2(\delta_{CN})$

experimental ones. It should be noted that we have obtained different assignments of the types of orbitals as compared to the assignments by Stefest and Bock [9] as well as those obtained by the X_α method [12]. The structure of the malononitrile anion obtained by MNDO with full geometry optimization was found to be planar; in comparison to malononitrile the C–C bonds are significantly shortened. The dissociation energy for malononitrile,

$$CH_2[CN]_2 \rightleftarrows \bar{C}H[CN]_2 + H^+,$$

calculated by MNDO is 1473.6 kJ/mol and is close to a measured value from so-called intrinsic acidity 1385.0 kJ/mol [13].

The above comparison shows that the transitivity of one-center atomic parameters assumed by Dewar and Thiel [6] works satisfactorily in the case of malononitrile. The MNDO method should thus be helpful in the investigation of the structure and reactivity of nitriles.

Optimal Energetical Path of Malononitrile Dimerization

A minimum-energy path (MEP) is usually considered to be the projection onto the coordinate-space plane of the line on a potential energy surface (PES) running in either direction from the saddle point along the valley bottoms toward the reactant and product minima. This path reflects the shape of the PES which is dependent upon the coordinates used to describe the system. However, this pseudo-minimum energy path MEP may conveniently provide an approximate indication of the energetics and structural changes occurring during the course of the reaction because the critical point on the PES (minima and saddle points) are independent of the choice of coordinates [14]. One popular method involves selection of a distinguished coordinate which changes monotonically and in a reasonably wide range during the reaction [15]. This coordinate is appropriately incremented and at each point the energy of the system is minimized with respect to the remaining internal degrees of freedom. In our case the distance between carbon $C2_M$ of malononitrile and carbon $(C1_A)$ of the anion was chosen as the reaction coordinate. In order to determine the number of degrees of freedom, the dependence of the energy of malononitrile-malononitrile anion supermolecule upon rotation of the dihedral angle $H_A{-}C1_A{-}C2_M{-}N1_M$ for several bond lengths $C1_A{-}C2_M$ has been investigated (Figure 2). We can

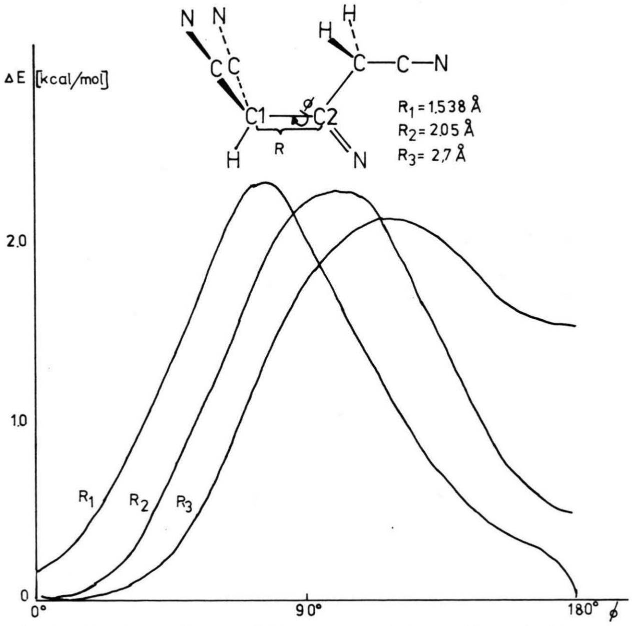


Fig. 2. The dependence of the energy of the malononitrile-malononitrile anion supermolecule upon the rotation of the dihedral angle H–C1–C2–N3 for several C1–C2 bond lengths.

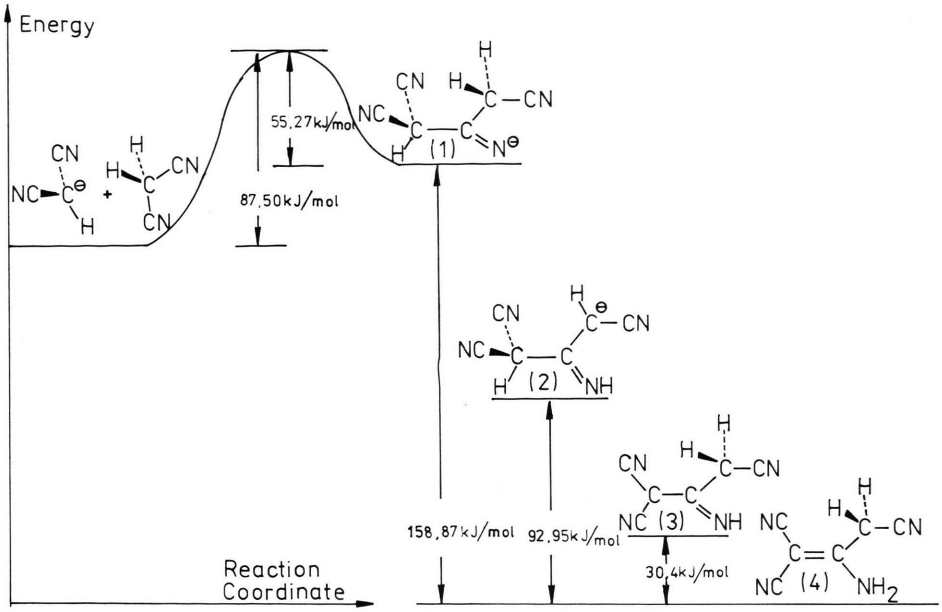


Fig. 3. Reaction profile for the reaction between the malononitrile and malononitrile anion, and relative stabilities of dimer anion tautomers.

see that in order to move along the valley bottom it should be assumed that H_A, $C1_A$, $C2_M$, $N1_M$ are planar. In order to simplify the calculations we assumed that the plane which passes though the atoms $C1_A$, $C2_M$, $C1_M$ is the mirror plane of the whole system. For this geometry the calculations were carried out beginning from $R_{C1_A-C2_M} = 1.589$ Å (equilibrium distance) to 3.0 Å with optimization of all other geometrical parameters. Figure 3 shows the reaction profile for this system with the $R_{C1_A-C2_M}$ distance as the reaction coordinate, and Figure 4 shows the geometries corresponding to the intermediate 1 and the transition state in Figure 3. For the large distance $R_{C1-C2} = 3.0$ Å, which corresponds to the separation of the malononitrile anion from the malononitrile molecule, the plane of the malononitrile anion is perpendicular to the plane passing through the nonhydrogenic atoms of malononitrile. This is an optimal geometry for nucleophilic attack of the malononitrile anion C1 sp^2 carbon onto the malononitrile carbon C2. We can see from Fig. 5 that the creation of the bond between the C1 and C2 carbon atoms is connected with the transfer of the excess charge from carbon $C1_A$ to nitrogen $N1_M$. Because the heat of formation of the dimer anion (1) is by about 128.5 kJ/mol greater than the heat of formation of the appropriate anion [3], the possibility of simultaneous proton transfer from $C1_A$ to $N3_M$ during $C1_A-C2_M$ bond formation has to be considered. When investigating the concomitant changes of the $H-C1_A-C2_M$ and $C1_A-C2_M-N3_M$ angles, the formation of the $C1_A-C2_M$ and $N3_M-H$ bonds, and the simultaneous breaking of the $C1_A-H$ bond, then the calculated energetical barrier rises to ca. 587.8 kJ/mol and seems to be too high for this hydrogen transfer to happen. The transition state appropriate to the synchronous reaction would be less polar than the transition states leading to the multi-step tautomeric transformations

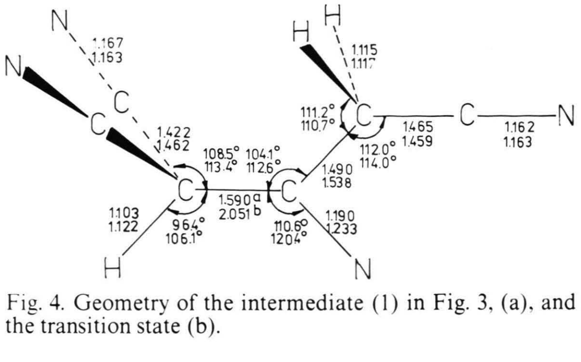


Fig. 4. Geometry of the intermediate (1) in Fig. 3, (a), and the transition state (b).

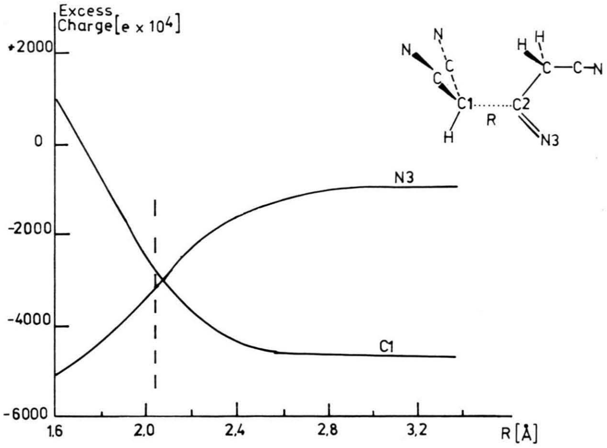
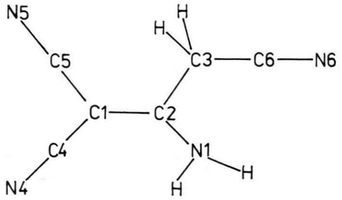


Fig. 5. Changes in the excess charge on carbon C1 and nitrogen N3 during C1−C2 bond formation.



	Ref. 16a	Ref. 16b	Ref. 16c	MNDO
C1−C2	1.382	1.377	1.394	1.381
C2−C3	1.501	1.507	1.504	1.530
C1−C4	1.422	1.423	1.424	1.428
C1−C5	1.421	1.409	1.429	1.428
C2−N1	1.313	1.308	1.317	1.403
C3−C6	1.458	1.456	1.470	1.457
C4−N4	1.141	1.137	1.141	1.162
C5−N5	1.151	1.145	1.146	1.162
C6−N6	1.133	1.135	1.139	1.161
C1−C2−C3	117.6°	118.1°		123.4°
C1−C2−N1	124.0°	123.6°		121.6°
C2−C3−C6	115.7	114.7		112.0°
C1−C5−N5	178.4°	178.9°		179.1°
C1−C4−N4	178.1°	179.3°		179.1°

Fig. 6. Calculated and experimental geometry of malononitrile dimer. Bond length in Å.

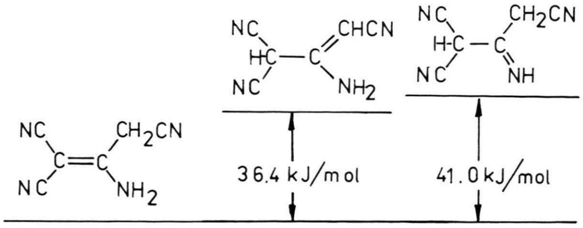


Fig. 7. The relative stability of malononitrile dimer tautomers.

that seem to be preferred. Also a 1,3 hydrogen shift subsequent to the formation of the dimer anion [1] must happen without participation of the polar surrounding and is expected to require a high activation energy; this route thus seems improbable in a strongly ionic reaction and polar medium with acidic hydrogen. The tautomeric transformation to the more stable tautomers, [3], [4], therefore probably passes through intermolecular interactions with water molecules or with other molecules of malononitrile, but not by an intramolecular process.

Ground State of Malononitrile Dimer

Geometrical parameters for the most stable tautomer of the malononitrile dimer are compared with the crystallographic data [16] in Fig. 6, the relative stability of tautomers for this dimer is shown in Figure 7. As with malononitrile, the agreement between calculated and experimental data is very good. The deviation in the calculated C2−N1 bond length compared to the crystal data is due to hydrogen bonding with nitrogen N1 in the crystal phase.

Acknowledgements

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[1] a) F. Freeman, Chem. Rev. **69,** 591 (1969); b) A. J. Fatiadi, Synthesis 165 (1978); c) F. Freeman, Chem. Rev. **80,** 329 (1980).

[2] G. W. Moore and J. F. Thorpe, J. Chem. Soc. **93,** 165 (1908).

[3] H. Inone, K. Hera, and I. Osugi, Rev. Phys. Chem. Japan **46,** 64 (1976).

[4] M. Miki, H. Yamagimachi, I. Kashiki, M. Sekei, and A. Suzuki, Hokkaido Daigaku Suisangakubu Kenkyn Iho **29,** 291 (1978), Chem. Abst. Vol. **91,** 92047.

[5] S. Bloch and G. Toupance, J. Chim. Phys. Phys.-Chim. Biol. **72,** 1157 (1975).

[6] M. J. S. Dewar and W. Thiel, J. Amer. Chem. Soc. **99,** 4899, 4907 (1977).

[7] a) E. Hirota and Y. Morino, Bull. Chem. Soc. Japan **33,** 705 (1960); b) E. Hirota, J. Mol. Spectr. **1,** 242 (1961); c) N. Muller and D. E. Pritchard, J. Amer. Chem. Soc. **80,** 3483 (1958).

[8] K. Obataka and S. Tanisaki, Phys. Lett. **A44,** 341 (1973).

[9] H. Stefest and H. Bock, Z. Naturforsch. [b] **28,** 746 (1973).

[10] T. Koopmans, Physica (Utrecht) **1,** 104 (1934).

[11] M. J. S. Dewar, Y. Yamaguchi, S. Doraiswamy, S. D. Sharma, and S. H. Suck, Chem. Phys. **41,** 21 (1979).

[12] J. Weber, N. Thalmar, and E. Haselbach, Chem. Phys. Lett. **57,** 230 (1976).

[13] T. B. McMahon and P. Kebarle, J. Amer. Chem. Soc. **98,** 3399 (1976).

[14] M. C. Flanigan, A. Komornicki, and J. W. McIver in Modern Theoretical Chemistry Vol. **9,** G. A. Segal, Ed. Plenum Press, New York 1977, p. 1.

[15] M. J. Rothman and L. L. Lohr, Chem. Phys. Lett. **70,** 405 (1980).

[16] a) B. Klawe, Acta Chim. Scand. **25,** 1999 (1971); b) B. Klawe, Acta Chim. Scand. **26,** 732 (1972); c) D. E. Zacharias, Dissertation Univ. Pittsburgh 1969, Diss. Abstr. Int. **B 30,** 1077 (1969).