

Ring-Opening Polymerization of Substituted 3,4-Dihydro-2H-pyrans. Syntheses of Alternating Vinyl Copolymers of Dimethyl Dicyanofumarate and Electron-Rich Olefins

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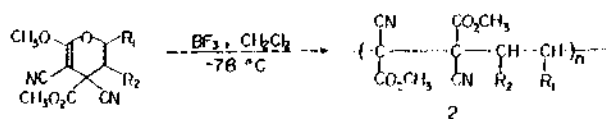
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Substituted 3,4-dihydro-2H-pyrans (**1**_n) were prepared by (4+2) cycloaddition reaction of dimethyl dicyanofumarate with the corresponding electron-rich olefins. The compounds **1**_n were ring-open polymerized by cationic initiators to obtain polymers of 1:1 alternating sequence. Polymerizations were carried out with boron trifluoride etherate in methylene chloride at -78°C. All the polymers obtained were soluble in common solvents and were reprecipitated by pouring its chloroform solution into diethyl ether. All the compounds **1**_n were not as reactive as the corresponding pyrans derived from α-cyanoacrylate.

Introduction

Extensive attention has been paid to the syntheses of vinyl polymers having alternating structure and several methods are suggested.¹⁻⁶ One of the methods which we have reported is ring-opening polymerization of substituted pyrans.^{7,8} This work is now extended to the construction of 1:1 alternating copolymers of another kind of vinyl monomers. The present report describes the syntheses and ring-opening polymerization of substituted 3,4-dihydro-2H-pyrans which lead to alternating copolymers of dimethyl dicyanofumarate and electron-rich olefins.

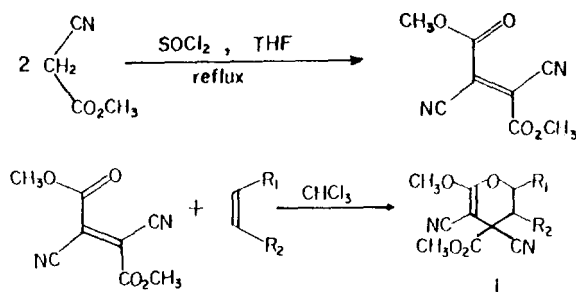


- 1
1a, 2a: R₁ = OCH₂CH₃, R₂ = H
1b, 2b: R₁ = p-CH₃OC₆H₅, R₂ = H
1c, 2c: R₁ = C₆H₅, R₂ = H
1d, 2d: R₁ = OCH₂CH₂CH₂CH₃, R₂ = H
1e, 2e: R₁ = p-CH₃OC₆H₅, R₂ = CH₃

Scheme I

Results and Discussion

Monomers **1a-e** were prepared according to the procedure similar to that reported already⁹ from dimethyl dicyanofumarate and the corresponding electron-rich olefins (Scheme II). Dimethyl dicyanofumarate was prepared in high yield by the reaction of methyl cyanoacetate with thionyl chloride in



Scheme II

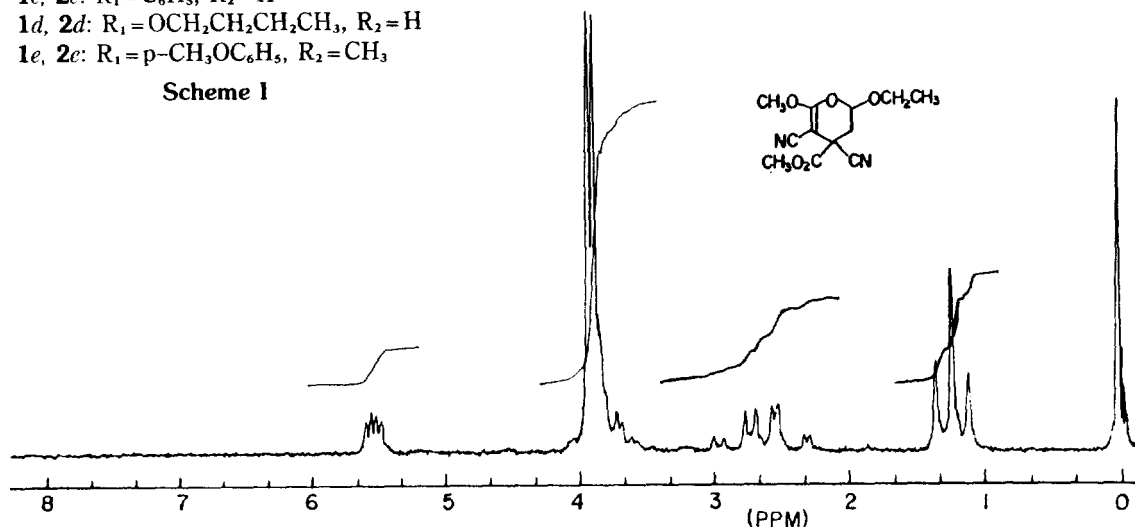


Figure 1. 60 MHz ¹H-NMR spectrum of methyl 2-ethoxy-6-methoxy-4,5-dicyano-3,4-dihydro-2H-pyran-4-carboxylate (**1a**) taken in CDCl₃ at room temperature.

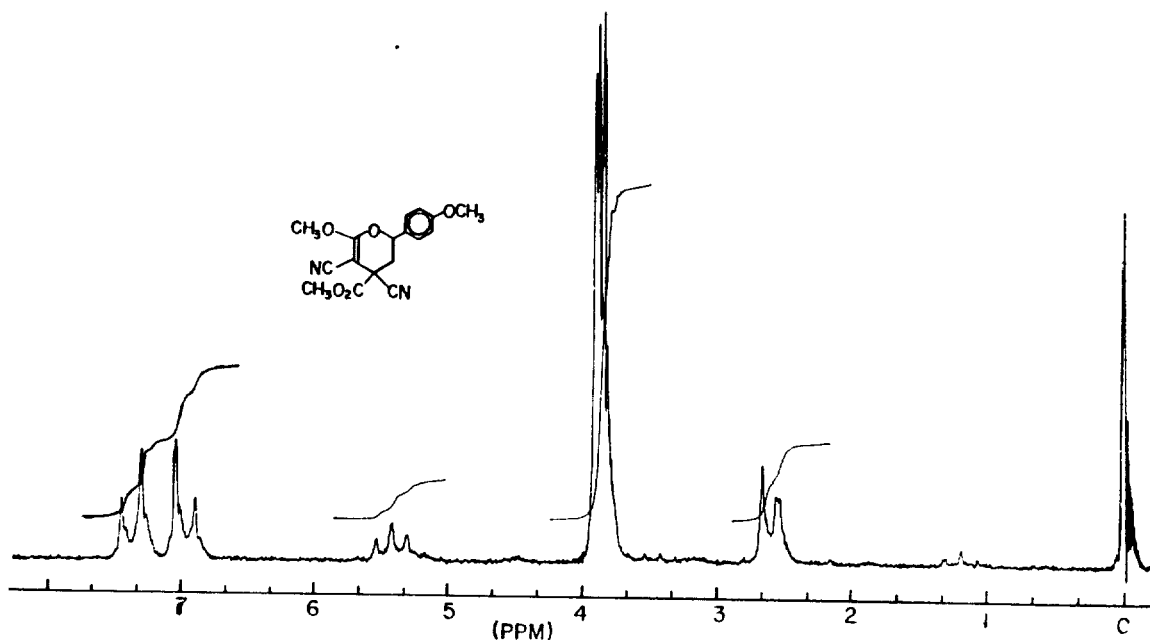


Figure 2. 60 MHz $^1\text{H-NMR}$ spectrum of methyl 2-(*p*-methoxyphenyl)-6-methoxy-4,5-dicyano-3,4-dihydro-2H-pyran-4-carboxylate (**1b**) taken in CDCl_3 at room temperature.

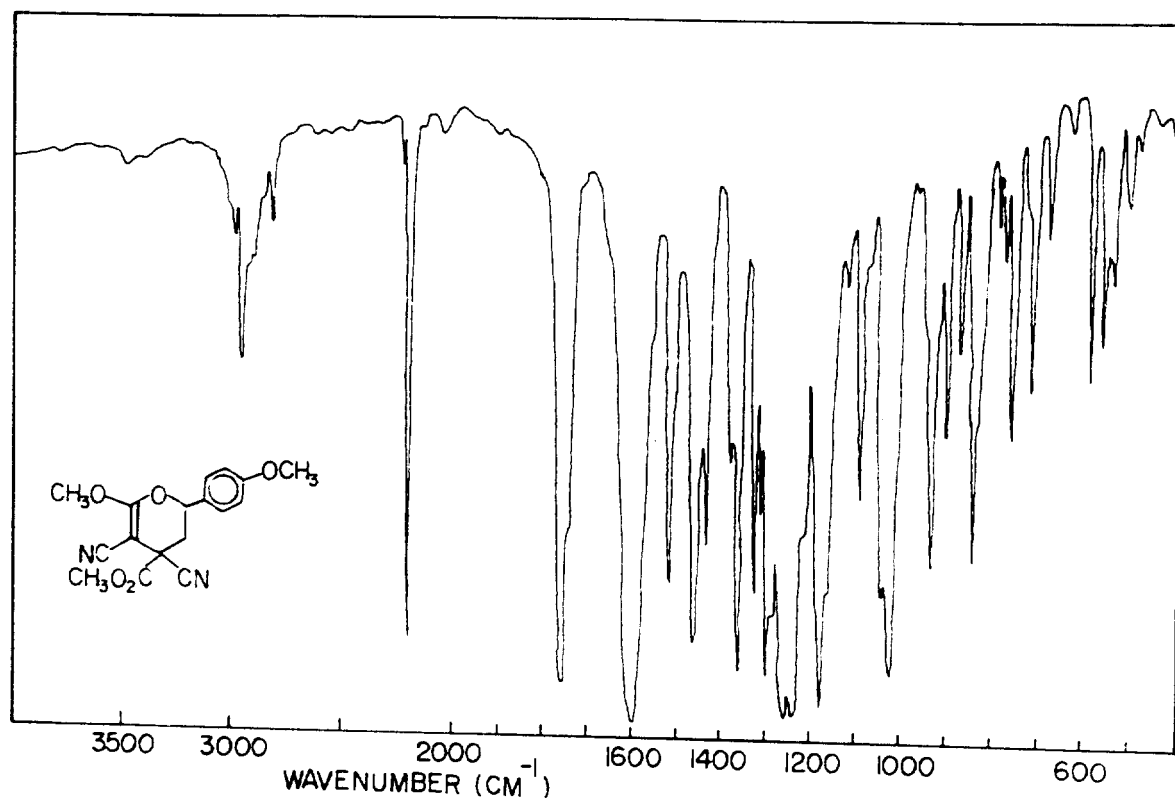


Figure 3. IR spectrum of methyl 2-(*p*-methoxyphenyl)-6-methoxy-4,5-dicyano-3,4-dihydro-2H-pyran-4-carboxylate (**1b**).

tetrahydrofuran.¹⁰ The chemical structures of the reaction products were identified by $^1\text{H-NMR}$ (Figure 1 and Figure 2) and IR spectra (Figure 3). All the spectral data confirmed the expected structures.

Polymerizations were carried out with BF_3 in dry CH_2Cl_2 at -78°C (Scheme I). All the polymers were soluble in common solvents such as chloroform and acetone, and were reprecipitated by pouring its chloroform solution into diethyl

Table 1. Cationic Ring-Opening Polymerization* of Substituted 3,4-Dihydro-2H-pyrans 1... under Various Conditions

monomer	solvent	monomer/ solvent, g/ml	initiator** to monomer, mol %	temp. °C	time, h	yield of product polymer, %	η_{inh} , dl/g***
1 _a	CH ₂ Cl	0.40	1.0	-78	20	50	0.12
1 _a	CHCl ₃	0.50	1.1	-30	48	45	0.11
1 _a	CH ₂ Cl ₂	0.30	1.2	-78	26	44	0.10
1 _a	CHCl ₃	0.33	1.4	-30	72	42	0.10
1 _a	CH ₂ Cl ₂	0.33	1.5	-78	96	26	0.08
1 _a	CHCl ₃	0.38	1.4	-30	72	21	0.08
1 _a	CHCl ₃	0.50	1.5	-30	96	24	0.06
1 _a	CHCl ₃	0.33	1.8	-30	144	16	~

*The copolymer compositions were estimated to be 1:1 by ¹H-NMR and IR spectra. **Initiator: Boron trifluoride etherate. *** Concentration of 0.5 g/dl in chloroform at 20°C.

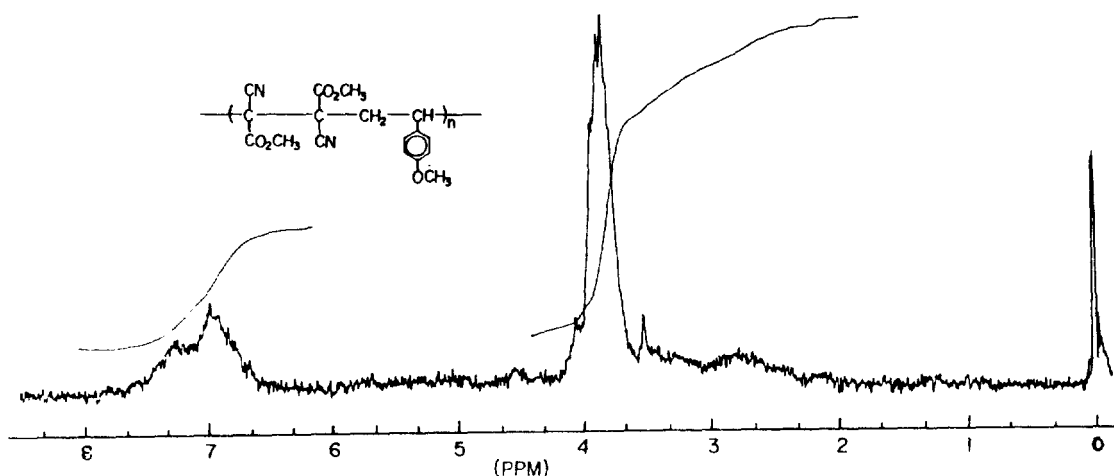


Figure 4. 60 MHz ¹H-NMR spectrum of alternating copolymer of dimethyl dicyanofumarate and p-methoxystyrene (2b).

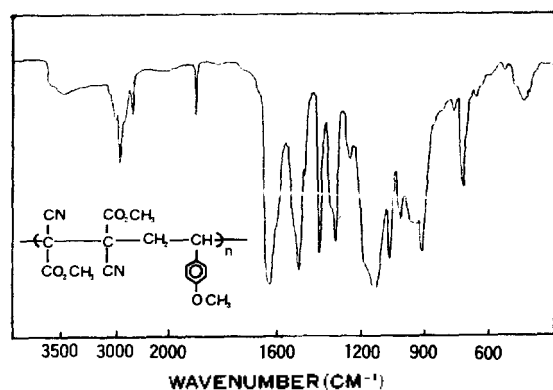


Figure 5. IR spectrum of alternating copolymer of dimethyl dicyanofumarate and p-methoxystyrene (2b).

ether. The experimental results are summarized in Table 1. The values in Table 1 show that the compounds 1 were not as reactive as some of the 2,6-dialkoxy-5-cyano-3,4-dihydro-2H-pyrans which we have reported previously,⁷ and the inherent viscosities of the polymers were rather low.

The chemical structures of the polymers were determined by ¹H-NMR (Figure 4) and IR spectra (Figure 5). The ¹H-NMR spectrum of polymer 2b shows resonance peak attributable to methyl protons at $\delta = 3.6 - 4.0$ (9H, 3 OCH₃). The signals of benzene ring protons are observed at $\delta = 6.6 - 7.4$. The polymer sample showed absorption bands at 1760 and 2240 cm⁻¹ indicating the presence of carbonyl and nitrile groups respectively. These spectral data indicate that the polymer contains both of the monomeric units.

It is rather well known that steric hindrance prevents the formation of highly substituted vinyl polymers in the ordinary polymerization conditions. Thus, dimethyl dicyanofumarate does not homopolymerize thermally or catalytically. However, since it is a planar structure, it copolymerized with electron-rich styrenes such as p-methoxystyrene and p-methylstyrene at 150 °C to give low molecular weight alternating copolymers in a low yield.¹¹ These alternating vinyl copolymers also can be prepared by a cationic polymerization of properly substituted pyrans investigated in the present report. Thus, we have found another synthetic method that lead to alternating copolymers of dimethyl dicyanofumarate and electron-rich ethylenes by a ring-opening fashion. According to our ex-

perience the highly substituted pyrans **1a-e** are much less reactive than some of 2,5,6-trisubstituted pyrans toward a cationic ring-opening polymerization. However, 2,3,5,6-tetrasubstituted-3,4-dihydro-2H-pyrans are ring-open polymerizable and the polymerizability is comparable to the 2,5,6-trisubstituted pyrans.¹²

We are exploring further the polymerization of other substituted pyrans and a full account of the work will be reported on shortly.

Experimental

Materials. The reagent grade chemicals were purified by distillation or recrystallization before use. Tetrahydrofuran was purified by refluxing over LiAlH_4 , and distilled under nitrogen. Chloroform was washed with water to remove ethanol and refluxed with phosphorus pentoxide, followed by fractional distillation. Methylene chloride was dried with anhydrous CaCl_2 , distilled over anhydrous CaSO_4 . Acetonitrile was purified by refluxing over calcium hydride, followed by fractional distillation. Boron trifluoride etherate was treated with a small amount of diethyl ether and distilled under reduced pressure. Ethyl vinyl ether and *n*-butyl vinyl ether were dried over sodium metal and distilled under vacuum. *p*-Methoxystyrene and styrene were distilled from calcium hydride under reduced pressure before use. Anethole was obtained from Fluka and used without further purification.

Measurements. All measured temperatures were uncorrected. IR spectra were taken on a Hitachi Model 260-30 infrared spectrophotometer. $^1\text{H-NMR}$ spectra were obtained on a Varian Model T-60A spectrometer (60 MHz). Melting points were taken on a Buchi 512 melting point apparatus.

Dimethyl dicyanofumarate. Dimethyl dicyanofumarate was prepared by the method of Ireland¹⁰ from methyl cyanoacetate and thionyl chloride in tetrahydrofuran. The product was recrystallized from dry methanol. 17.5g (53% yield): mp 176-177°C; $^1\text{H-NMR}$ (CDCl_3) δ 4.05 (s, 2 CH_3); IR (KBr) 1740 ($\text{C}=\text{C}$) cm^{-1} .

Methyl 2-ethoxy-6-methoxy-4,5-dicyano-3,4-dihydro-2H-pyran-4-carboxylate (1a). Ethyl vinyl ether (2.2g, 0.03 mol) was added slowly to the chloroform (30 ml) solution of dimethyl dicyanofumarate (3.5g, 0.018 mol). The reaction mixture was stirred at room temperature for 48 hours. Solvent and excess ethyl vinyl ether were then removed under reduced pressure, and the resulting product was dissolved in a cold diethyl ether (20 ml). The solution is placed in a refrigerator (-20°C) to crystallize. White crystal was collected and washed a few times with cold diethyl ether to give **1a**: 4.32g (90.4% yield): mp 110-112°C; $^1\text{H-NMR}$ (CDCl_3) δ 1.27 (t, 3H), 2.30-3.03 (m, 2H), 3.70-3.95 (m, 8H), 5.55 (m, 1H); IR (KBr) 2200 ($\text{C}\equiv\text{N}$), 1760 ($\text{C}=\text{O}$), 1600 ($\text{C}=\text{C}$) cm^{-1} .

Methyl 2-(*p*-methoxyphenyl)-6-methoxy-4,5-dicyano-3,4-dihydro-2H-pyran-4-carboxylate (1b). *p*-Methoxystyrene (2.68g, 0.02 mol) was added carefully to the chloroform (10 ml) solution of dimethyl dicyanofumarate (1.94g, 0.01 mol). The mixture was stirred at 65°C for 20 hours. The red color which was developed initially disappeared during the reaction. After evaporation of solvent and excess *p*-methoxystyrene by rotary evaporator the resulting product was dissolved in 20 ml of cold diethyl ether. The solution was placed in a refrigerator. The precipitated white product was collected by suction filtration and washed a few times with

cold diethyl ether to obtain **1b**: 2.69g (82% yield): mp 124-125°C; $^1\text{H-NMR}$ (CDCl_3) δ 2.55-2.66 (d, 2H), 3.70-3.90 (m, 9H), 5.40 (t, 1H), 6.85-7.43 (m, 4H); IR (KBr) 2200 ($\text{C}\equiv\text{N}$), 1760 ($\text{C}=\text{O}$), 1600 ($\text{C}=\text{C}$) cm^{-1} .

Methyl 2-phenyl-6-methoxy-4,5-dicyano-3,4-dihydro-2H-pyran-4-carboxylate (1c). Styrene (2.08g, 0.02 mol) was added to the acetonitrile (20 ml) solution of dimethyl dicyanofumarate (1.94g, 0.01 mol). The mixture was stirred at 70°C for 20 hours. The color of the solution changed to yellow during the reaction. The precipitated white polymer was separated by suction filtration, and the filtrate was concentrated by rotary evaporator. The resulting yellowish product was dissolved in a cold diethyl ether (15 ml). The solution is placed in a refrigerator (-20°C). White product was collected and washed a few times with cold diethyl ether. **1c**: 1.25g (41.9% yield): mp 125-126°C; $^1\text{H-NMR}$ (CDCl_3) δ 2.25-2.65 (d, 2H), 3.75-3.90 (m, 6H), 5.40 (t, 1H), 7.40 (s, 5H); IR (KBr) 1745 ($\text{C}=\text{O}$), 1605 ($\text{C}=\text{C}$) cm^{-1} .

Methyl 2-*n*-butyl-6-methoxy-4,5-dicyano-3,4-dihydro-2H-pyran-4-carboxylate (1d). *n*-Butyl vinyl ether (2.0g, 0.02 mol) was added to the acetonitrile (20 ml) solution of dimethyl dicyanofumarate (2.34g, 0.012 mol). The reaction mixture was stirred at 60°C for 12 hours. Solvent and excess *n*-butyl vinyl ether were removed under vacuum to give **1d**: 1.31g (91% yield): $^1\text{H-NMR}$ (CDCl_3) δ 0.80-1.10 (m, 3H), 1.18-1.72 (m, 4H), 2.17-2.78 (m, 2H), 3.82-3.95 (m, 8H), 5.54 (m, 1H); IR (neat) 2200 ($\text{C}\equiv\text{N}$), 1750 ($\text{C}=\text{O}$), 1620 ($\text{C}=\text{C}$) cm^{-1} .

Methyl 2-(*p*-methoxyphenyl)-3-methyl-6-methoxy-4,5-dicyano-3,4-dihydro-2H-pyran-4-carboxylate (1e). Anethole (2.22g, 0.015 mol) was added to the chloroform (20 ml) solution of dimethyl dicyanofumarate (1.94g, 0.01 mol). The mixture was stirred at 65°C for 20 hours. After evaporation of solvent the resulting product was standing at room temperature to crystallize for 2 days. White solid product was collected and washed a few times with cold diethyl ether, followed by suction filtration and drying. **1e**: 3.02g (88.0% yield): mp 126-128°C (lit.¹³ 125-128°C); $^1\text{H-NMR}$ (CDCl_3) δ 1.88 (d, 3H), 2.38-2.86 (m, 1H), 3.78-3.96 (m, 9H), 5.05 (d, 1H), 6.85-7.38 (q, 4H); IR (KBr) 2200 ($\text{C}\equiv\text{N}$), 1740 ($\text{C}=\text{O}$), 1610 ($\text{C}=\text{C}$) cm^{-1} .

Cationic Polymerization of 1. A representative cationic polymerization procedure (the case of **1a**) was as follows: A solution of **1a** (1.33g, 0.05 mol) was placed in a rubber septum stopper capped pyrex glass ampoule under nitrogen. The resulting solution was flushed with dry nitrogen for 30 minutes. The ampoule was then placed in dry ice-acetone bath under nitrogen, and 0.02 ml of boron trifluoride etherate was added to the solution. After 20 hours the ampoule was taken out and the polymerization mixture was poured into a large volume of diethyl ether. The precipitated white polymer was collected and reprecipitated from chloroform into diethyl ether. Thus obtained polymer was then dried in a vacuum oven at 30°C. **2a**: 0.67g (50% yield); η_{inh} = 0.12 dl/g (c, 0.5 g/dl in chloroform at 20°C).

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Location of Transition States by the Conjugate Reaction Coordinate Method

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A relatively simple method of locating the saddle point is presented. In this method a single determination of the saddle point location by constrained energy minimizations for points selected on the assumed saddle surface provides us with the structure, location and energy of the TS, the reaction path at the saddle point and characterization as the TS. Some examples were given.

Introduction

The determination of transition states (TS) plays a central role in visualizing and predicting mechanisms of chemical rate processes, since they represent saddle points between the two local minima on energy surfaces corresponding to reactants and products. The experimental determination of TS geometries, however, is extremely difficult; the theoretical determination also presents great difficulties albeit various computational methods of saddle point location have been proposed.¹⁻⁴

In this paper we report a relatively simple method for locating the saddle point (T) from which the TS itself can be obtained. The method automatically characterizes the TS by determining two rectangular coordinate axes (with origin at the saddle point T) representing the reaction path, ξ , (reaction coordinate, RC) and the direction orthogonal to it, η , (orthogonal coordinate, OC) on the saddle surface of the hyperbolic paraboloid (eq. 1) shown in Figure 1.

$$\epsilon(\xi, \eta) = A\xi^2 + B\eta^2 \quad (1)$$

where $A < 0$ and $B > 0$

Method

The potential energy E of a molecule depends on a set of molecular coordinates $\{q_i\}_{i=1}^n$, and a constrained minimum energy surface with respect to the two, x and y, can be expressed as

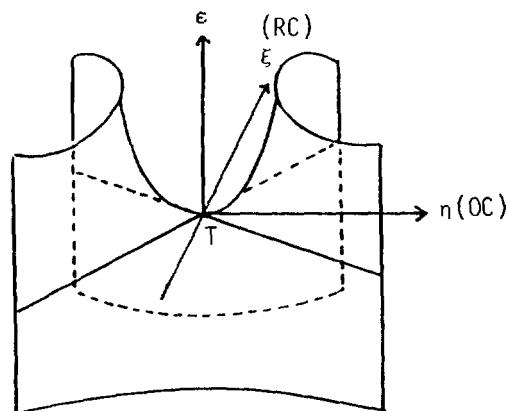


Figure 1. Hyperbolic paraboloid potential energy surface, $\epsilon = A\xi^2 + B\eta^2$, where $A < 0$ and $B > 0$, showing the reaction coordinate(ξ) and the orthogonal coordinate(η) with the origin at the saddle point(T).

$$E(x, y) = \min. \{E(q_1, q_2, \dots, q_{n-2}, x, y)\} \quad (2)$$

The energy E(x,y) defines a minimum energy surface in the sense that the molecular system is constrained to achieve an energy minimum regarding the remaining n-2 coordinates.

A saddle point on this surface should satisfy the following conditions.⁵

$$(i) \quad \frac{\partial E}{\partial q_i} = 0 \quad \text{for all coordinate } i, \quad (3a)$$