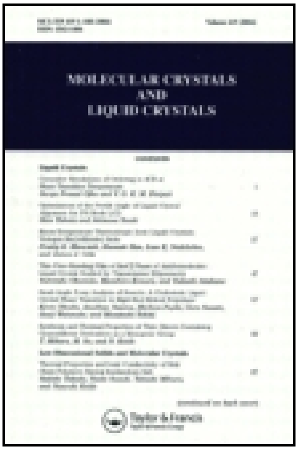

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Helmut Gross [a] & Hans Sixl [a]
[a] Physikalisches Institut, Teil 3, Universität Stuttgart, D-7000 Stuttgart 80, West Germany

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SPECTROSCOPY OF THE INTERMEDIATES OF THE LOW TEMPERATURE POLYMERIZATION REACTION IN DIACETYLENE CRYSTALS

HELMUT GROSS AND HANS SIXL
Physikalisches Institut, Teil 3, Universität
Stuttgart, D-7000 Stuttgart 80, West Germany

Abstract We report on the physical and chemical properties of the photoproduct series obtained in the low temperature photopolymerization reactions of diacetylene crystals. The initiation, the addition and chain termination reactions are discussed. A one-dimensional electron gas model is applied to the optical absorption series of the diradical and asymmetric carbene intermediates as well as on the stable oligomer molecules. A reaction model of the photopolymerization reaction in diacetylene crystals is presented.

INTRODUCTION

In a solid state reaction large dimension monomer diacetylene single crystals are converted to polymer single crystals with high perfection[1,2]. The class of diacetylene crystals represents a unique model system for the study of reaction mechanisms, characterized by a variety of reaction intermediates[3-6]. This unconventional reactivity and the resulting unusual physical properties of the polymer crystal have attracted the interest of both, physicists and chemists. Up to now the best investigated diacetylene crystals with the monomer molecular structure $R-C\equiv C-C\equiv C-R$ are the TS-6 crystals with substituents $R=CH_2SO_3C_6H_4CH_3$.

The photochemical primary processes of this extraordinary low temperature reaction are shown schematically in Figure 1 by example of the diradical DR-series. The photoinitiation reaction is a two step reaction[6,7]. The first step of this reaction involves an electronic excitation of a monomer molecule M to a reactive diradical configuration M*. In a second step the central carbon atoms of the adjacent molecule must be distorted into a position most appropriate for the chemical reaction to the dimer molecule by a vibrational excitation $\tilde{M}$. The photoaddition reaction from the dimer to the trimer etc. is a one step reaction, which is performed by the same vibrational excitation $\tilde{M}$. At low temperature all excitations M* and M are obtained by absorption of photons.

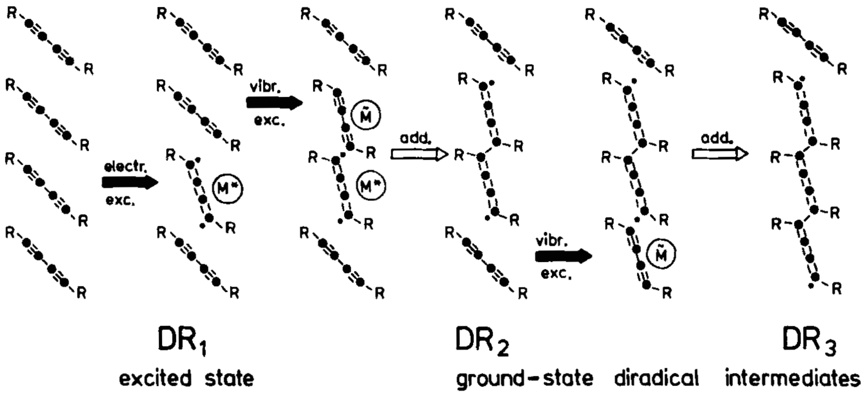

FIGURE 1. Reaction scheme of the photopolymerization reaction in diacetylene crystals.

In this paper we present the optical absorption spectra of the low temperature photoproducts, which are obtained during the polymerization reaction of diacetylene crystals. The chemical structures of the intermediates and final photoproducts are shown in Figure 2. The diradical DR intermediates and the dicarbene DC intermediates have two reactive chain ends. The asymmetric carbene AC intermediates are obtained after a first chain termination reaction. Finally stable oligomer SO photoproduct absorptions are obtained after a second chain termination reaction.

The specific radical and carbene structures of the intermediates have been identified unambiguously by ESR spectroscopy. Only the proposed pseudo-

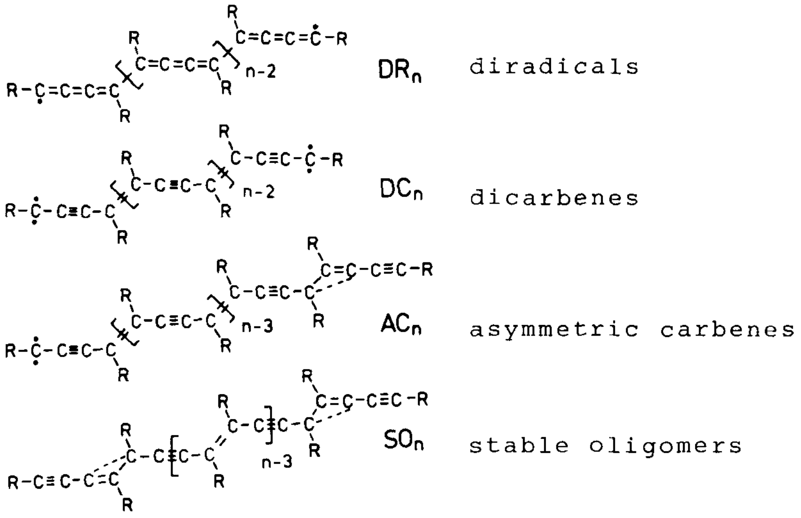

FIGURE 2. Chemical structures of the low temperature photoproducts in diacetylene crystals.

cyclopropene structure resulting from the termination reactions is hypothetical.

The positions of the different optical absorption series will be described by a one-dimensional electron model. Information concerning the specific butatriene $\{RC{=}C{=}C{=}CR\}_n$ or acetylene (ynene) structure $\{RC{-}C{\equiv}C{-}CR\}_n$ of the photoproducts and of the polymer molecules are obtained. The individual reaction steps of the low temperature photoreaction will be presented. A reaction model is deduced from the non-linear intensity dependence of the dimer initiation. The reaction mechanisms of the primary photochemical reactions at low temperature will be discussed.

OPTICAL ABSORPTION SPECTRA

The polarized optical absorption spectra of the DR, AC and SO low temperature photoproducts of Figure 2 are shown in the spectra (1) to (5) of Figure 3. The first step in the preparation of all spectra is the UV-photoinitiation of the dimer A-molecules

FIGURE 3. Optical absorption spectra of the DR_n, AC_n and SO_n low-temperature photoproducts in diacetylene crystals with electric field vector of the incident light polarized parallel to the chain axis.
(1) Effect of the one excimer laser pulse.
(2) After addition reaction of (1).
(3) After optical bleaching of (1).
(4) After addition reaction of (3).
(5) After optical bleaching of (2).

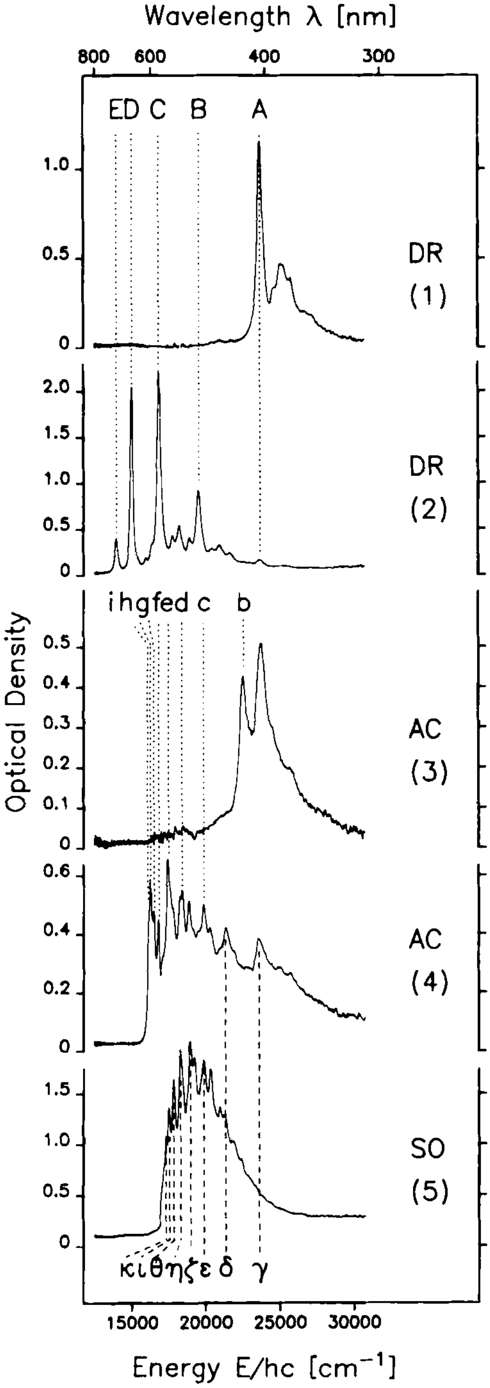
Wavelength λ [nm]
800
600
400
300
E D C B A
i h g f e d c b
κ ι θ η ζ ε δ γ
Optical Density
1.0
0.5
0
2.0
1.5
1.0
0.5
0
0.5
0.4
0.3
0.2
0.1
0
0.6
0.4
0.2
0
1.5
1.0
0.5
0
DR (1)
DR (2)
AC (3)
AC (4)
SO (5)
15000
20000
25000
30000
Energy E/hc [cm⁻¹]

FIGURE 3

(spectrum (1)) with zero-phonon absorption at 420 nm using one excimer laser UV-pulse (Lambda Physics EMG 100). Spectrum (2) then is obtained by thermal addition reaction steps within the diradical series A → B → C... at about 100 K. Spectrum (3) shows the result of optical bleaching of the dimer A-absorption of spectrum (1) by resonant irradiation using a xenon high pressure arc and a 420 nm interference filter. In this reaction asymmetric carbene intermediates b and stable oligomer molecules γ are formed according to the photoreaction A → b → γ. Spectrum (4) is obtained by optical addition reaction steps within the asymmetric carbene series b → c → d... Finally the unreactive stable oligomer absorptions of spectrum (5) are obtained by optical bleaching of the whole DR series of spectrum (2) via the reactions $DR_n \rightarrow AC_{n+1} \rightarrow SO_{n+2}$.

The correlation of the A, B, C,... photoproduct absorption series to diradical DR intermediates and the correlation of the b, c, d,... photoproduct absorption series of asymmetric carbene AC intermediates is based on the ESR fine structure and hyperfine structure analysis[4] and on their reaction kinetics[6]. The correlation of the γ, δ, ε,... series to unreactive stable oligomer SO molecules is based on their thermal and optical stability. The correlation to dimer, trimer, tetramer... molecules follows from the chemical reaction sequences observed in the time resolved optical and ESR measurements[6,8] and from the following calculations.

CALCULATION OF THE SPECTRAL POSITIONS

A simple one-dimensional electron gas theory is applied on the absorption series observed in the optical experiments. The explicit dependence of the optical absorption series of a linear one-dimensional conjugated chain of length l is given by[9]

$$E_n = (h^2/8ml^2)(4n+1) + E_\infty(1-1/4n) \qquad (1)$$

with $l = a_1 n + a_2$; h and m are Plancks constant and the electron mass, respectively. a_1 is given by the length of the repetition unit and a_2 describes the boundary conditions at the ends of the oligomers.

The zero-phonon line positions of the DR_n, AC_n and SO_n photoproducts are summarized in Figure 4. The excellent fit of the theoretical curves

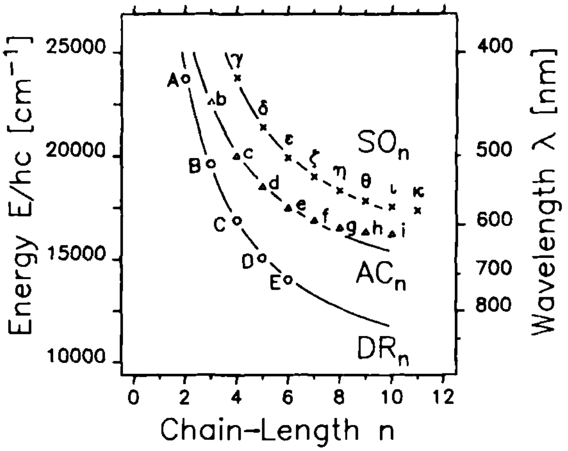

FIGURE 4. Chain-length dependence of the photoproduct series. The calculated curves have been fitted to the experimental points.

to the experimental points shown in Figure 4 by variation of only a_2 and E_∞ supports the correlation of the different DR, AC and SO photoproducts to distinct chain lengths n in monomer units. There are neither excess nor missing intermediates.

The convergence energies E_∞ of the AC and SO series for $n \rightarrow \infty$ are closest to the absorption energy of the polymer chain (E_p = 17000 cm^{-1}) and consequently are suspected of having related structures. However, the convergence of the DR series A, B, C,... is strongly red shifted in comparison with the absorption of the polymer. The diradicals DR shown in Figure 2 differ essentially from the other intermediates by their butatriene structure. Consequently the modulation of the one-dimensional potential is changed. The modulation is determined by the differences in the bond lengths within the carbon backbone arising from the bond alternation. In the absence of any bond alternation E_∞ goes to zero! Therefore the convergence energy E_∞ is strongly affected by the different bond structures of the individual photoproduct series.

The radical or carbene chain end structures, deduced from the ESR experiments are only consistent with a butatriene structure of the DR series and with an acetylene structure of the AC series. Owing to the close relationship between the polymer absorption and the E_∞ value of the AC-series an acetylene structure of the final polymer chain is deduced. This is in accordance with the proposed acetylene structure of the long polymer chains, as deduced originally from the X-ray structure data[10].

As shown by ESR experiments[6] the butatriene structure is favoured energetically as compared to the acetylene structure only at short chain lengths corresponding to the photoproducts A to E. Longer butatrienic photoproducts F, G, H,... and the corresponding ESR and optical absorptions have not been detected in the TS-6 crystals. Moreover the ESR spectra give clear evidence that the diradical intermediates are transformed to the dicarbene intermediates of Figure 2 at a critical chain lengths of $n_c = 6$ according to the reaction $DR_6 \rightarrow DC_7$. The series of dicarbene DC intermediates is only observed in the ESR spectra[4,6]. Due to their enormous length ($n \geq 7$) and to a small oscillator strength we have not been able, up to now, to localize their corresponding optical absorption individually and independent of the polymer absorptions.

DIMER INITIATION REACTION

In the photoinitiation reaction by one laser pulse only dimer diradicals are produced as shown in spectrum (1) of Figure 3. Corresponding to our reaction model presented in Figure 1 two light quanta hν are required in the bimolecular reaction of two monomer molecules M corresponding to the reaction equation

$$M + DR_n \overset{h\nu}{\rightleftarrows} [MDR_n]^* \rightarrow AC_{n+1} \qquad (2)$$

The kinetical equations corresponding to the above dimer initiation reaction after laser pulse excitation are given by[11]

$$d[M^*]/dt = -k^*[M^*] - k_2[M^*][\tilde{M}],$$
$$d[\tilde{M}]/dt = -\tilde{k}[\tilde{M}],$$
$$d[M_2]/dt = +k_2[M^*][\tilde{M}]. \qquad (3)$$

$[M^*]$, $[\tilde{M}]$ and $[M_2]$ are the concentrations of the metastable monomer diradical DR_1, of the distorted monomer molecules $\tilde{M}$ and of the stable dimer diradical DR_2 molecules. k^* and $\tilde{k}$ are the first order non-chemical decay constants of the M^* and $\tilde{M}$ molecules. k_2 is the second order rate constant of the chemical dimer initiation reaction.

Figure 5 shows the intensity dependence of the integral M_2 optical absorption of the dimer diradi-

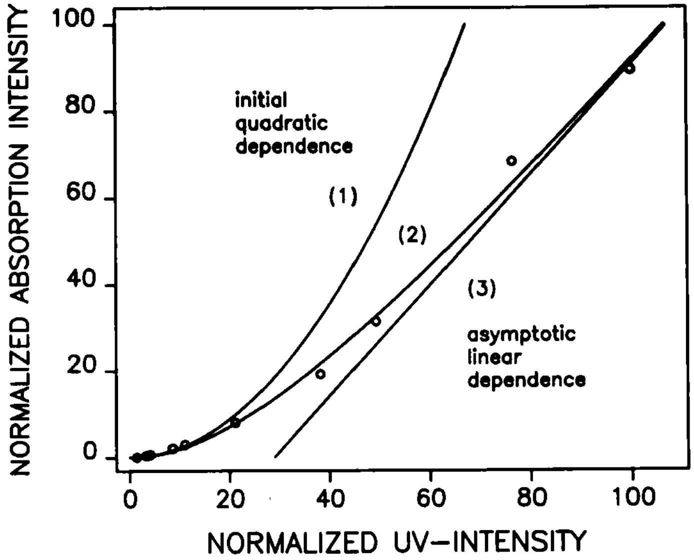

FIGURE 5. Intensity dependence of the dimer initiation reaction.

cal photoproduct A. The non-linear dependence has been fitted using the solutions[11] of the kinetical equations (3). The normalized axes correspond to $6 \cdot 10^{14}$ photons per mm^2 and to a concentration of $5 \cdot 10^{12}$ dimers per mm^2. At low laser power a quadratic intensity dependence is observed in contrast to the linear intensity dependence at high laser power. The calculated curve is fitted to the experimental points. A quantum yield of one dimer molecule per 100 photons is obtained in the linear high-intensity limit.

In contrast to the two-quantum mechanism of the low-temperature photodimerization process, the formation of a polymer chain at high temperatures is the result of a one-photon chain-initiation event, followed by thermally activated chain growth[7,11]. Above ≈ 200 K the $\tilde{M}$ states of Figure 1 and Eqs. (2) and (3) become thermally activated and independent of the time resulting in a linear intensity dependence of the polymerization reaction.

OPTICAL CHAIN TERMINATION REACTIONS

In a first chain termination reaction of the diradical molecules the reactive radical electrons at one chain end are destroyed. The type of the intermediates is changed upon addition of a monomer molecule. The resulting transformation reactions

$$M + DR_n \overset{h\nu}{\rightleftarrows} [MDR_n]^* \rightarrow AC_{n+1} \qquad (4)$$

are most efficient by resonant irradiation into the respective DR_n absorptions as shown for example by the generation of the b-absorption (spectrum (3)) of Figure 3 via optical bleaching of the A-absorption (spectrum (1)). A quantitative analysis has been performed in Figures 6 (a) and (b) by example of the D → e reaction, showing an exponential decay of the D-absorption and the corresponding exponential rise of the e-absorption. The absorption intensities of the AC absorptions are

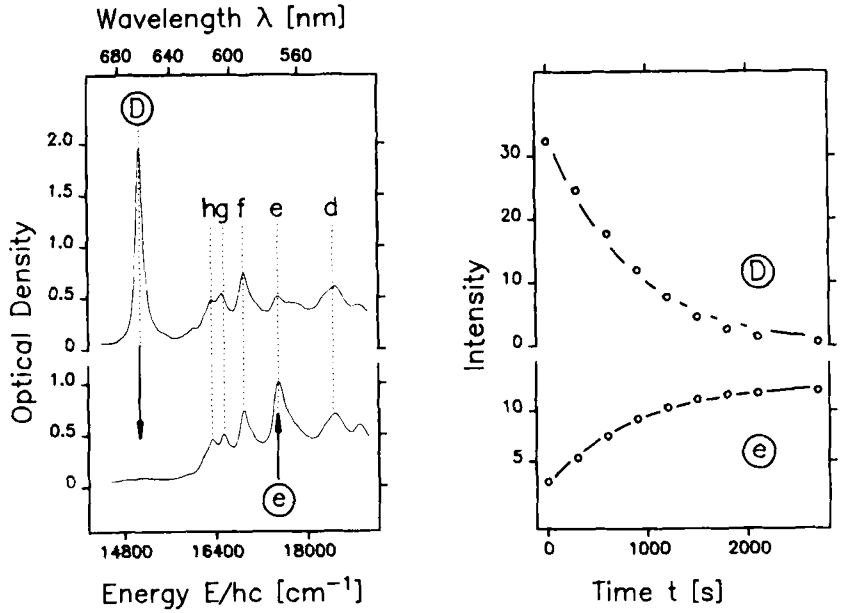

FIGURE 6. Resonant optical bleaching.

(a) The upper and lower curves show the spectra before and after optical bleaching with λ=660 nm.

(b) Time dependence of the intensities during optical bleaching generally lower than those of the DR absorptions. This is due to a change of the oscillator strength by a factor of 1/3.

In a second chain termination reaction the reactive carbene electrons of the other chain end are destroyed following

$$M + AC_n \overset{h\nu}{\rightleftarrows} [MAC_n]^* \rightarrow SO_{n+1}. \qquad (5)$$

In this final termination reaction the unreactive SO molecules are produced.

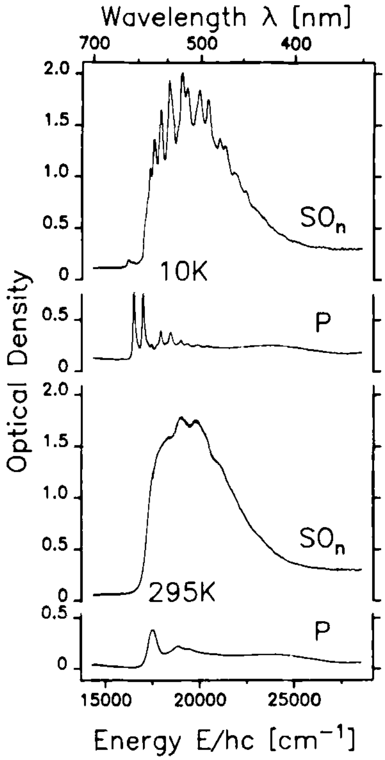

FIGURE 7. High and low temperature spectra of the polymer P and stable oligomer SO_n molecules.

For comparison the spectra of the stable oligomer molecules SO_n are shown in Figure 7 together with the polymer P absorptions at high and at low temperatures. The SO_n series is obtained by the procedure described in Figure 3. The polymer absorption is generated by thermal polymerization of the TS-6 crystal at room temperature.

CHAIN ADDITION REACTIONS

The chain propagation within the reactive DR, DC or AC series is performed by addition of the adjacent monomer molecules. The excitation into their reactive $\tilde{M}$ state is possible both optically and thermally. At low temperatures (T < 80 K) only optical addition reactions are observed. Above 100 K the thermal addition reactions become very important and are faster than 1 µs at 300 K[8]. The addition reactions are summarized by the following equations

$$M + DR_n \overset{h\nu \text{ or } kT}{\rightleftarrows} \tilde{M}DR_n \rightarrow DR_{n+1},$$

$$M + DC_n \overset{h\nu \text{ or } kT}{\rightleftarrows} \tilde{M}DC_n \rightarrow DC_{n+1},$$

$$M + AC_n \overset{h\nu \text{ or } kT}{\rightleftarrows} \tilde{M}AC_n \rightarrow AC_{n+1}. \qquad (6)$$

In the addition reactions the type of the intermediates is conserved with the only exception of the thermal transformation of the diradicals to the dicarbenes at $n_c = 6$. The probability of an addition reaction step upon excitation of $\tilde{M}$ is much higher than that of the corresponding chain termination reactions. The probabilities of the optical and thermal chain termination reactions are below 30% and 5%, respectively.

SUMMARY

The complexity of the primary processes in the solid state polymerization reaction has been demonstrated in this paper by the manifold of different reaction products and multiple reaction pathways. The spectroscopic interest has been focussed mainly on the reaction properties of the optical absorption series of the different short chain photoproduct series. The mechanisms of the photoinitiation, of the optical and thermal chain propagation and of the chain termination reactions have been successfully investigated, due to the stability of the reactive intermediates at low temperatures. A model calculation of the absorption series is in accordance with the different chain structures of the photoproducts shown in Figure 2. The diradicals differ by their dominant butatriene structure from the rest of the photoproducts and from the final polymer structure, which are predominantely determined by their acetylene structure.

From the experimental results and conclusions, drawn from the investigation of the TS-6 model system, we may be able to derive general characteristics of the polymerization reaction in diacetylene crystals. This is due to the fact, that the intermediates are not directly dependent on the

specific structure and chemical properties of the substituents[12]. Differences in the polymerization reactions essentially arise from the specific molecular arrangements, resulting in specific changes of the distances and orientations of the reactive centers of the individual molecules.

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