Chinese Chemical Letters Vol. 12, No. 12, pp 1131 – 1134, 2001
http://www.imm.ac.cn/journal/ccl.html


# Crystal Structure of Diethyl [2,3-Di(Ethoxycarbonyl)-2, 3-di(*p*-nitrophenyl)] Succinate

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**Abstract:** A new conformational carbon-carbon bond free radical initiator diethyl [2,3-di(ethoxycarbonyl)-2,3-di(*p*-nitrophenyl)] succinate (EMNPS) was synthesized and identified by elemental analysis, FAB-MS, IR and $^1$H NMR spectroscopy. The analytical results of single crystal X-ray show the conformation of EMNPS tends to be a stagger gauche form, and torsion angle of the two gauche phenyls is smaller than 60°. There is obvious elongation in central carbon-carbon bond length (0.161 nm). EMNPS can be decomposed into two relatively stable free radicals measured by ESR. By initiating bulk polymerization of methyl methacrylate (MMA), EMNPS shows the ability of controlling the molecular weight of polymers.

**Keywords:** Diethyl [2,3-di(ethoxycarbonyl)-2,3-di(*p*-nitrophenyl)] succinate, synthesis, crystal structure, "living" free radical polymerization.

Controlled free radical polymerization (CFRP) is an effective means to synthesize polymers of predetermined molecular weight, narrow molecule weight distribution and well-defined architecture. One of the most important milestones in the development of CFRP was the discovery of the iniferter (initiation-transfer-termination) reactions[1]. Iniferter avoids ordinary bimolecular termination and undergoes initiation, chain transfer to the initiator, and primary radical termination, so it may initiate "living" free radical polymerization. Many compounds such as organic sulfur compounds[2], azobisdiphenylmethane[3], and thiuram disulfides[4] can serve as iniferters for the polymerization of vinyl monomers. 2,2,3,3-tetra-substituted succinate derivatives[5,6] are capable of acting as iniferters of "living" free radical polymerization owing to the substituted groups. In order to study the structure basis of these compounds as iniferters of "living" free radical polymerization in more details, a new iniferter diethyl [2,3-di(ethoxycarbonyl)-2,3-di(*p*-nitro phenyl)] succinate has been synthesized and its crystal structure was measured. It shows significant controlling on the molecular weight of PMMA in the bulk polymerization of MMA initiated by EMNPS.

## Experimental

*Synthesis of Diethyl 2-(p-nitrophenyl)malonate*

Diethyl 2-(*p*-nitrophenyl)malonate was prepared following the literature method[7]. The general process is the same as literatures. But *p*-nitrochlorobenzene was used instead of *p*-nitrobromobenzene. Yield: 58.0%. mp 56-57°C[7].

*Synthesis of EMNPS*

14.05 g (0.05 mol) diethyl 2-(nitrophenyl) malonate dissolved in 50 mL methanol was added into a 100 mL round bottle equipped with a stirrer, thermometer, trickling filler and refluxing condenser. Then 16.47 g (0.05 mol) $K_3Fe(CN)_6$ dissolved in 20 mL thick ammonia were added slowly and heated for 24 hours and cooled to the temperature range of 35-40°C. The cooled mixture was diluted with 20 mL 2mol/L HCl solution and extracted with 3×15 mL $CH_2Cl_2$. The organic layer was dried over $MgSO_4$ overnight. Removal of $CH_2Cl_2$ gave a dense liquid. Crystallization from methanol gave 2.78 g colorless crystals. Yield: 10%. mp 142-143°C. Elemental Analysis $C_{26}H_{28}N_2O_{12}$: Calculated (%), C 55.71, H 5.00, O 34.29; Found (%), C 55.37, H 4.64, N 5.00, O 34.43. $^1$H NMR ($CDCl_3$, TMS), δ/ppm 1.23-1.29 (t, J = 6.91, 12H), 4.28 - 4.32 (q, J = 6.98, 8H), 7.14-7.19 (d, J = 8.75, 4H), 7.94-7.98 (d, J = 9.17, 4H). MS (*m/z*): 583 (M+23).

*Preparation and measurement of Single Crystal*

The crude compound was washed and dissolved in methanol. With the evaporation of solvent a colorless single crystal was prepared.

The single-crystal X-ray experiments were performed on a Brüker P4 deffractometer equipped with graphite monochromatized Mo $K_\alpha$ radiation. At room temperature (294±1K), data collection was monitored by three standards every 100 reflection collected. Bond lengths, angles, and other crystal parameters were obtained.

*Polymerization of MMA initiated by EMNPS*

A solution of 0.48 mmol EMNPS in 24 mL MMA in six tubes was heated at 90°C under nitrogen. After intervals the viscous solution was added to 20 mL methanol. The PMMA was purified and dried. Then measure molecular weights and get the relations of conversion-time and of mv-conversion.

## Results and Discussion

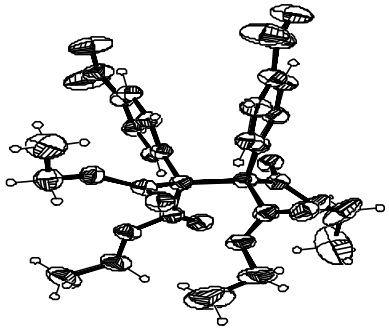
With the effects of stereo-hindrance and electron withdrawing of substituted groups, the central carbon-carbon bond length of 1,1,2,2-tetra-subs tituted-1,2-diphenylethane is elongated.

**Table 1** The bond lengths around the central carbon atoms (nm)

| Bonds | 1 | 2 | normal values |
|---|---|---|---|
| C $(sp^3)_{central}$-C (Ph) | 0.1543 | 0.1547 | 0.1511 |
| C $(sp^3)_{central}$-C (COOR) | 0.1546 | 0.1542 | 0.1447 |
| | 0.1554 | 0.1547 | |
| C $(sp^3)_{central}$-C $(sp^3)_{central}$ | 0.1605 | | 0.1544 |

Compared with diisobutyl 2,2-dicyano-2,3-diphenyl succinate (DBCPS)[8], EMNPS shows a stagger gauche form. The torsion angle of two nitrophenyl groups (got from Newmamm projection) is 54.7°, while in DBCPS the angle is about 180°. All these results illustrate that there is obvious stereo-hindrance between large substituted groups linked to central carbon.

**Figure 1** ORTEP drawing of EMNPS

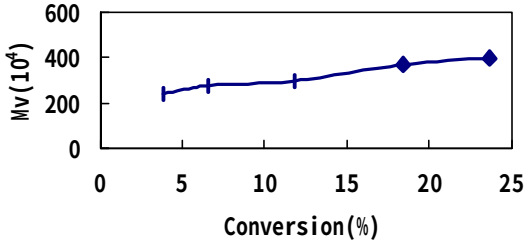


The three pairs of groups linked to central carbon have a strong electron withdrawing ability. In the result, the electron cloud density of central carbon-carbon bond is reduced (according to literature[9], the main factor is perhaps not due to the effect of $-NO_2$ group). With the effect of all these factors, the compound has a high energy level and is easily decomposed to stable free radicals. It is confirmed by ESR. Also, this is the exact structural basis of initiating free radical polymerization.

When EMNPS was used as the initiator of bulk polymerization of MMA, we got the following relation. The conversion increased as the polymerization going on. Also, it shows the molecule weight of PMMA increased as conversion increased. This

is one of the main characters of "living" free radical polymerization. It shows EMNPS can probably be used as iniferter of free radical polymerization.

**Figure 2** The Relation of Mv-Conversion of MMA initiated by EMNPS at 90°C, [EMNPS]=0.02M.




## Acknowledgment

We appreciate Professor Ru Ji Wang for his help in measurement and explaining of crystal structure.

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Received 25 April, 2001